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(54) Title: COPOLYESTERS AND POLYMERIZATION OF MACROCYCLIC OLIGOESTERS

(57) Abstract: Copolyesters have been prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst and from oligoesters and organotin compounds with or without the presence of a transesterification catalyst. The invention generally features a method of making a copolyester, a method of making a block copolymer of polyester, and a copolyester.

## COPOLYESTERS AND POLYMERIZATION OF MACROCYCLIC OLIGOESTERS

### Technical Field

[0001] This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to copolyesters and their preparation from macrocyclic oligoesters.

### Background Information

5 [0002] Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a  
10 dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding.

[0003] Recently, macrocyclic oligoesters were developed which have unique properties. These properties make them attractive as matrices for engineering thermoplastic composites. The  
15 desirable properties stem from the fact that macrocyclic oligoesters exhibit low melt viscosity, allowing them easily to impregnate a dense fibrous preform followed by polymerization to polyesters. Furthermore, certain macrocyclic oligoesters melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally.

20 [0004] Despite the above-described properties and other advantages, some of the resulting polyesters prepared from macrocyclic oligoesters may display a high crystallinity that invariably diminishes the favorable properties including the polymer's ductility. Thus, methods are needed for preparing polyesters with favorable crystallinity and ductility while retaining the advantages of using macrocyclic oligoesters as precursors to polyesters.

25 [0005] In addition, the required volume ratio of a macrocyclic oligoester to a conventional catalyst (e.g., non-polymeric organotin compounds or titanate esters) is very high, typically greater than 100:1 in order to attain a satisfactory molecular weight of the product. See, e.g.,

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U.S. Patent No. 5,466,744 to Evans *et al.* Sophisticated and costly metering and mixing equipment is used to introduce and disperse properly the relatively small amount of catalyst.

[0006] Furthermore, typical non-polymeric organotin compounds are volatile enough to raise health concerns. Stable non-volatile organotin catalysts are needed.

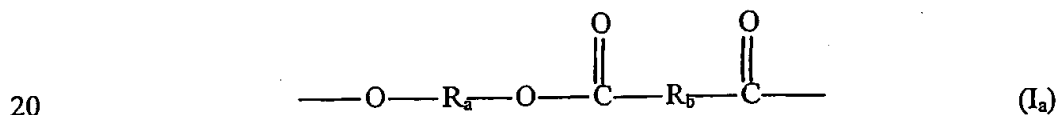
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#### Summary of the Invention

[0007] Copolyesters of high molecular weight are prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst. The copolyesters so prepared show favorable crystallinity and ductility while retaining other desirable properties of polyesters prepared from macrocyclic oligoesters as precursors.

10 [0008] Copolyesters containing organotin moieties also are prepared from macrocyclic oligoesters and organotin compounds. The organotin-copolyesters so prepared can be used as polymerization catalysts. The organotin-copolyesters are non-volatile macromolecules and contain less tin per unit volume than the original organotin compounds. Thus, it requires substantially lower volume ratio of macrocyclic oligoester to the polymerization catalyst.

15 [0009] In one aspect, the invention generally features a method of making a copolyester. In one embodiment, the method includes the steps of providing a macrocyclic oligoester, providing a cyclic ester other than a macrocyclic oligoester, and contacting the macrocyclic oligoester and the cyclic ester in the presence of a transesterification catalyst at an elevated temperature to produce a copolyester. The macrocyclic oligoester has a structural repeat unit of formula (I<sub>a</sub>):



where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group.

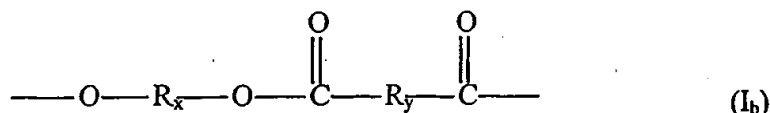
[0010] In another aspect, the invention generally features a method of making a block copolymer of polyesters. In one embodiment, the method includes contacting a macrocyclic oligoester and a transesterification catalyst at an elevated temperature to form a first polymeric segment. Subsequently contacting the first polymeric segment, a cyclic ester that is not a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps then are sequentially repeated a desired number of times to form a block copolyester having additional first and second polymeric segments.

30 [0011] In another embodiment that is a variation of the above method of making a block copolymer, a first polymeric segment is formed by contacting a cyclic ester that is not a

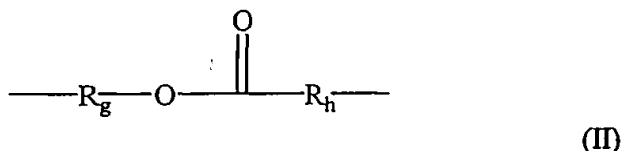
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macrocyclic oligoester and a transesterification catalyst at an elevated temperature. Subsequently contacting this first polymeric segment, a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps then are sequentially repeated a desired number of times to form a block copolymer having additional first and second polymeric segments.

[0012] In yet another aspect, the invention features a composition that is a copolyester. In one embodiment, the copolyester contains, within its polymeric backbone, at least one structural unit of formula (I<sub>b</sub>)



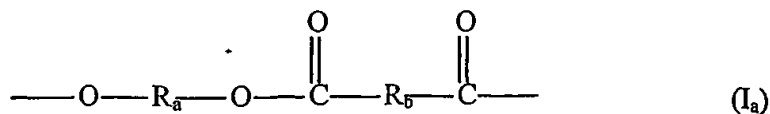
where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a divalent aromatic or alicyclic group; and at least one structural unit of formula (II)



where R<sub>g</sub> and R<sub>h</sub> are independently an organic moiety with the proviso that R<sub>g</sub> is not -O-R<sub>x</sub>- if R<sub>h</sub> is -R<sub>y</sub>-C(O)-. R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group. R<sub>y</sub> is a divalent aromatic or alicyclic group.

[0013] In yet another aspect, the invention features a block copolymer of polyesters. A first block unit of the copolymer has, within its polymeric backbone, at least one first structural unit of formula (I), as defined above. A second block unit has, within its polymeric backbone, at least one second structural unit of formula (II), as defined above.

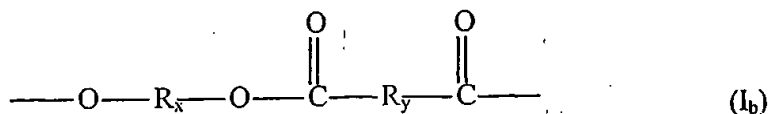
[0014] In yet another aspect, the invention features a method for making a copolyester. In one embodiment, the method includes the steps of providing an oligoester, providing a non-catalytic amount of an organotin compound, and contacting the oligoester and the organotin compound at an elevated temperature to produce an organotin-copolyester. In one embodiment, the oligoester has a structural repeat unit of formula (I<sub>a</sub>):



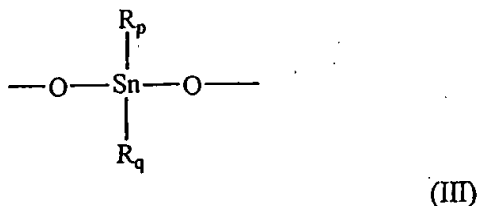
where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group.

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[0015] In yet another aspect, the invention features a copolyester. In one embodiment, the copolyester includes, within its polymeric backbone, at least one structural unit of formula (I<sub>b</sub>)

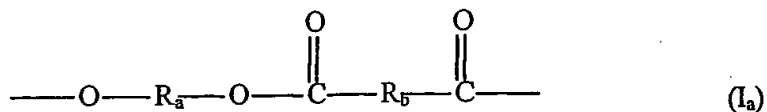


where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a  
5 divalent aromatic or alicyclic group; and at least one structural unit of formula (III)

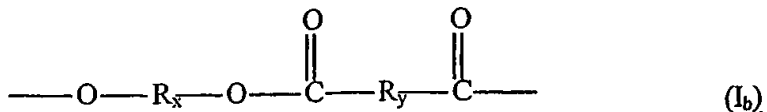


where each of R<sub>p</sub> and R<sub>q</sub> independently is a halogen atom or an alkyl group.

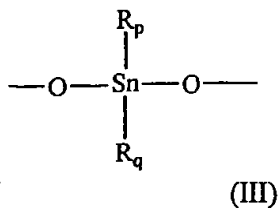
[0016] In yet another aspect, the invention features a method for polymerizing a macrocyclic oligoester. In one embodiment, the method includes the steps of providing a macrocyclic  
10 oligoester, providing a polymerization catalyst, and contacting the macrocyclic oligoester and the polymerization catalyst at an elevated temperature thereby producing a copolyester. The macrocyclic oligoester includes a structural repeat unit of formula (I<sub>a</sub>):



where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a  
15 divalent aromatic or alicyclic group. The polymerization catalyst includes at least one component compound each of which has a formula that includes (i) at least one structural unit of formula (I<sub>b</sub>)



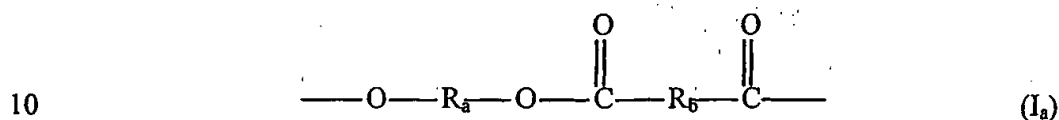
where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a  
20 divalent aromatic or alicyclic group; and (ii) at least one structural unit of formula (III)



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where each of  $R_p$  and  $R_q$  independently is a halogen atom or an alkyl group.

[0017] In yet another aspect, the invention features a method for manufacturing a mixture of a macrocyclic oligoester and a polymerization catalyst. The mixture is substantially free from water. In one embodiment, the method includes the steps of mixing an oligoester and an  
 5 organotin compound, heating the mixture of the oligoester and the organotin compound at an elevated temperature, removing water generated during the heating step to obtain a dried reaction mixture of oligoester and organotin compound, and mixing the dried reaction mixture of oligoester and the organotin compound with the macrocyclic oligoester. The oligoester has a structural repeat unit of formula (I<sub>a</sub>):



where  $R_a$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and  $R_b$  is a divalent aromatic or alicyclic group.

[0018] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and claims.

15

### Description

[0019] The present invention is related to the surprising discovery that copolyesters having favorable crystallinity, ductility, non-volatility, catalytic activity, and/or tin content can be prepared from macrocyclic oligoesters, organotin compounds and/or cyclic esters with or without the presence of a transesterification catalyst.

20

### Definitions

[0020] The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

[0021] As used herein, a "macrocyclic" molecule means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form  
 25 the ring.

[0022] As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

[0023] As used herein, an "oligoester" means a molecule that contains 2 or more identifiable ester functional repeat units of the same or different formula. An oligoester typically refers to

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molecules that are intermediate in terms of the number of ester functional repeat units present in the molecule. However, an oligoester also may include molecules that contain large numbers of ester functional repeat units such that they may be classified as polyesters. In certain embodiments, an oligoester may refer to a macrocyclic oligoester as defined below.

5 [0024] As used herein, a "macrocyclic oligoester" means a macrocyclic oligomer containing 2 or more identifiable ester functional repeat units of the same or different formula. A macrocyclic oligoester typically refers to multiple molecules of one specific formula having varying ring sizes. However, a macrocyclic oligoester may also include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. A macrocyclic  
10 oligoester may be a co-oligoester or multi-oligoester, i.e., an oligoester having two or more different structural repeat units having an ester functionality within one cyclic molecule.

[0025] As used herein, a "cyclic ester" means a cyclic molecule having at least one ring within its molecular structure that contains an ester functionality within the ring. A cyclic ester typically refers to multiple molecules of one specific cyclic ester. A cyclic ester as used herein is not a  
15 macrocyclic oligoester as defined above.

[0026] As used herein, an "organotin compound" means an organic compound that contains one or more tin atoms covalently bound to at least one carbon atom.

[0027] As used herein, an "organotin ester" means an organotin compound that contains one or more tin-oxygen-carbon bonds.

20 [0028] As used herein, a "cyclic organotin ester" means an organotin ester that contains a cyclic structure. It should be understood that a cyclic organotin ester may contain one or more tin-oxygen-carbon bonds that may or may not be part of the cyclic structure.

[0029] As used herein, a "non-metal-containing cyclic ester" means a cyclic ester that does not contain atoms of metallic elements.

25 [0030] As used herein, "an alkylene group" means  $-C_nH_{2n}-$ , where  $n \geq 2$ .

[0031] As used herein, "a cycloalkylene group" means a cyclic alkylene group,  $-C_nH_{2n-x}-$ , where x represents the number of H's replaced by cyclization(s).

[0032] As used herein, "a mono- or polyoxyalkylene group" means  $[-(CH_2)_m-O-]_n-(CH_2)_m-$ , where m is an integer greater than 1 and n is an integer greater than 0.

30 [0033] As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

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[0034] As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure therein.

5 [0035] As used herein, a "block copolymer" means a copolymer having segments of two or more polymers linked to one another. A block copolymer has constitutionally different structural units. Adjacent segments (i.e., blocks) contain structural units derived from different characteristic species of monomer or from structural repeat units with different composition or sequence distribution.

10 [0036] As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as a fibrous or particulate material. Illustrative examples of particulate material are chopped fibers, glass microspheres, and crushed stone. Certain fillers and additives thus can be used to prepare polyester polymer composites. A fibrous material means more continuous substrate, e.g., fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

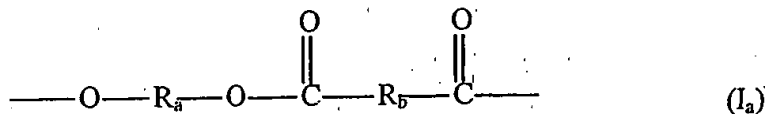
15 [0037] As used herein, "a divalent organic moiety" means any organic group so long as it does not interfere with the polymerization reaction of a macrocyclic oligoester and a cyclic ester. The organic moiety can be saturated or unsaturated. The organic moiety can be a hydrocarbon group or in addition can contain one or more heteroatoms. The organic moiety can be linear or branched, or contain one or more cyclic or heterocyclic structures containing one or more O, N, or S atoms. Exemplary divalent organic moieties include divalent mono- or polyalkylene groups  
20 containing 1-20 carbon atoms, cycloalkylene groups containing 1-20 carbon atoms, and substituted or unsubstituted divalent aromatic groups such as phenyl groups or alicyclic groups containing 1-20 carbon atoms.

#### **Preparation of Copolyesters from Macrocyclic Oligoesters and Cyclic Esters**

25 [0038] High molecular weight copolyesters have been prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst.

[0039] In one aspect, the invention generally features a method for making a copolyester. In one embodiment, the method includes the steps of providing a macrocyclic oligoester, providing a cyclic ester other than a macrocyclic oligoester, and contacting the macrocyclic oligoester and  
30 the cyclic ester in the presence of a transesterification catalyst at an elevated temperature to produce a copolyester. The macrocyclic oligoester has a structural repeat unit of formula (I<sub>a</sub>):

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where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group.

[0040] A polymerization reaction occurs between a macrocyclic oligoester and a cyclic ester.

- 5 The polymerization typically is completed within minutes. The duration of the polymerization reaction depends on many factors such as the molar ratio of macrocyclic oligoester to cyclic ester, the molar ratio of the ester monomers (the macrocyclic oligoesters and the cyclic esters) to catalyst, the temperature at which the polymerization reaction is carried out, the desired molecular weight of the product, and the choice of solvent. The polymerization is preferably
- 10 conducted under an inert environment, such as under nitrogen or argon, or under a vacuum.

- [0041] The molar ratio of cyclic ester to macrocyclic oligoester can vary from about 0.01:1 to 10:1. In one embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.1:1 to about 1:1. In another embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.1:1 to about 0.5:1. The molar ratio of ester monomers
- 15 (macrocyclic oligoester and cyclic ester combined) to the catalyst can range from about 20:1 to about 500,000:1. In one embodiment, the molar ratio of ester monomers to catalyst is from about 20:1 to about 10,000:1. In another embodiment, the molar ratio is about 50:1 to about 5,000:1. In yet another embodiment, the molar ratio is from about 200:1 to about 500:1.

- [0042] Yields of copolyesters depend on, among other factors, the precursor monomers
- 20 (macrocyclic oligoester and cyclic ester) used, the reaction conditions, and the work-up procedure. Typical yields range from about 90% to about 98%. The resulting copolyesters typically have molecular weights from about 90,000 to about 150,000. The temperature range of melting endotherm can be as low as about 145°C to about 180°C for high cyclic ester content to as high as about 200°C to about 230°C for low cyclic ester content. The peak temperature ranges
- 25 from about 165°C to about 220°C. The heat of melting is determined by differential scanning calorimetry (DSC) to be from about 10 to about 50 Joule/g.

- [0043] Copolyesters prepared according to methods of the invention show improved crystallinity and ductility as demonstrated by the temperature range of melting endotherm and the heat of melting of the resulting copolyesters. Copolyesters having a 40% caprolactone content,
- 30 for example, exhibit a drastically lowered melting point range and reduced heat of melting, indicative of low crystallinity and high ductility.

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[0044] The polymerization reaction may be carried out with or without a solvent. A solvent may be used to dissolve one or more of the reactants and/or to mix the reactants. A solvent may also be used as a medium in which the reaction is carried out. Illustrative solvents that may be used include high-boiling compounds such as *o*-dichlorobenzene and meta-terphenyl. In another embodiment, no solvent is used in the polymerization reaction.

[0045] Cyclic esters employed in various embodiments of the invention include any cyclic esters that react with a macrocyclic oligoester to form a copolyester under transesterification conditions.

[0046] Cyclic esters include lactones. The lactones may have any number of atoms within their ring. In one embodiment, lactones of 4-10-membered rings are used. The lactone can be unsubstituted or substituted. One or more carbon atoms in the lactone structure can be substituted with a heteroatom such as O, N, or S. One or more hydrogen atoms in the basic lactone structure can be substituted with a halogen atom (e.g., F, Cl, Br, or I) or other functional groups including alkyl groups (e.g., methyl, ethyl, propyl, butyl), a hydroxyl group, alkyloxy groups, a cyano group, amino groups, and aromatic groups. The lactone can contain one or more additional rings. Examples of lactones include lactide, glycolide, dioxanone, 1,4-dioxane-2,3-dione,  $\epsilon$ -caprolactone,  $\beta$ -propiolactone, tetramethyl glycolide,  $\beta$ -butyrolactone,  $\gamma$ -butyrolactone, and pivalolactone.

[0047] Catalysts employed in the invention are those that are capable of catalyzing a transesterification polymerization of a macrocyclic oligoester with a cyclic ester. As with state-of-the-art processes for polymerizing macrocyclic oligoesters, organotin and organotitanate compounds are the preferred catalysts, although other catalysts may be used. For example, an organotin compound, dibutyltin dioxide, can be used as polymerization catalyst. Other illustrative organotin compounds include 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, *n*-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-*n*-butyltin(IV) oxide and di-*n*-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as *n*-butyltin tri-*n*-butoxide, dialkyltin(IV) dialkoxides such as di-*n*-butyltin(IV) di-*n*-butoxide and 2,2-di-*n*-butyl-2-stanna-1,3-dioxacycloheptane, and trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.* In addition, tin catalysts described in commonly owned U.S.S.N. 09/754,943 (incorporated by reference herein in its entirety) may be used in the polymerization reaction.

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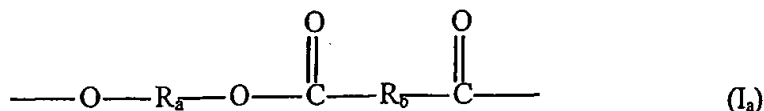
[0048] As for titanate catalysts, tetra-isopropyl titanate may be employed in the invention. Other examples of titanate catalysts include tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds described in commonly owned U.S.S.N. 09/754,943 (incorporated by reference herein in its entirety).

- 5 [0049] The polymerization reaction is carried out at an elevated temperature. In one embodiment, the temperature is maintained within a range from about 100°C to about 300°C, or from about 100°C to about 260°C, or from about 150°C to about 210°C, or from about 170°C to about 200°C, or from about 180°C to about 190°C.

#### 10 Preparation of Copolyesters from Macrocyclic Oligoesters and Organotin Compounds

[0050] Copolyesters, including low, medium, and high molecular weight copolyesters, have been prepared from macrocyclic oligoesters and organotin compounds, in the presence or absence of a transesterification catalyst.

- [0051] In one aspect, the invention generally features a method for making a copolyester. The method includes the steps of providing an oligoester, providing a non-catalytic amount of an organotin compound, and contacting the oligoester and the organotin compound at an elevated temperature to produce a copolyester. In one embodiment, the oligoester has a structural repeat unit of formula (I<sub>a</sub>):



- 20 where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group.

- [0052] A polymerization reaction occurs between an oligoester and an organotin compound. The polymerization typically is completed within about a few minutes to about an hour. The duration of the polymerization reaction depends on many factors such as the molar ratio of oligoester to the organotin compound, the temperature at which the polymerization reaction is carried out, the desired molecular weight, the presence or absence of a catalyst (other than the organotin compound itself), and the choice of solvent. The polymerization is preferably conducted under an inert environment, such as under nitrogen or argon, or under a vacuum.

- [0053] The organotin compound is provided in a non-catalytic amount, which is an amount greater than what typically is used when the compound is employed as a catalyst. The organotin compound here is employed as a reactant, although it may also serve as a catalyst at the same

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time. The molar ratio of oligoester to organotin compound typically varies from about 500:1 to about 0.5:1. In one embodiment, the molar ratio of oligoester to organotin compound is between about 100:1 to about 0.5:1. In another embodiment, the molar ratio of oligoester to organotin compound is between about 50:1 to about 1:1. In yet another embodiment, the molar ratio of

5 oligoester to organotin compound is between about 10:1 to about 1:1.

[0054] Yields of the copolyesters depend on, among other factors, the precursor oligoesters and organotin compounds employed, the reaction conditions, and the work-up procedure. Yields range from about 85% to about 99% based on monomer units. Typically, the yield ranges from about 90% to about 99%.

10 [0055] The resulting copolyesters typically have weight average molecular weights from about 1,000 to about 200,000. In one embodiment, the resulting copolyester has a weight average molecular weight from about 1,000 to about 150,000. In another embodiment, the resulting copolyester has a weight average molecular weight from about 2,000 to about 120,000. In yet another embodiment, the resulting copolyester has a weight average molecular weight from about  
15 2,000 to about 50,000. In yet another embodiment, the resulting copolyester has a weight average molecular weight from about 50,000 to about 120,000.

[0056] Copolyesters prepared according to methods described here have several advantageous properties. As will be more fully discussed later, the copolyesters can be transesterification catalysts themselves, and may be used in the polymerization of macrocyclic oligoesters. As  
20 stable polymers, these macromolecular catalysts have essentially no vapor pressure. Thus, they do not raise health concerns as do conventional non-polymeric catalysts. In addition, the tin concentration of these macromolecular catalysts are reduced so that the amount of catalyst needed to achieve the same tin content is increased. In conventional systems, the catalyst to monomer ratio is typically 1:100 or less. The copolyesters of the invention, in contrast, allow a  
25 ratio of as high as 1:10 to 1:3. The higher ratio of catalyst to macrocyclic oligoesters allows easy introduction and mixing of reactants. A need for sophisticated metering equipment is therefore reduced or even eliminated.

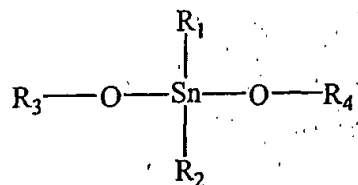
[0057] The polymerization reaction may be carried out with or without a solvent. A solvent may be used to dissolve one or more of the reactants and/or to mix the reactants. A solvent may  
30 also be used as a medium in which the reaction is carried out. Illustrative solvents that may be used include high-boiling compounds such as *o*-dichlorobenzene and meta-terphenyl. In another embodiment, no solvent is used in the polymerization reaction.

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[0058] Organotin compounds that may be employed in various embodiments of the invention include any organotin compounds that react with an oligoester to form a copolyester under transesterification conditions.

[0059] Organotin compounds that may be used in the invention include organotin esters.

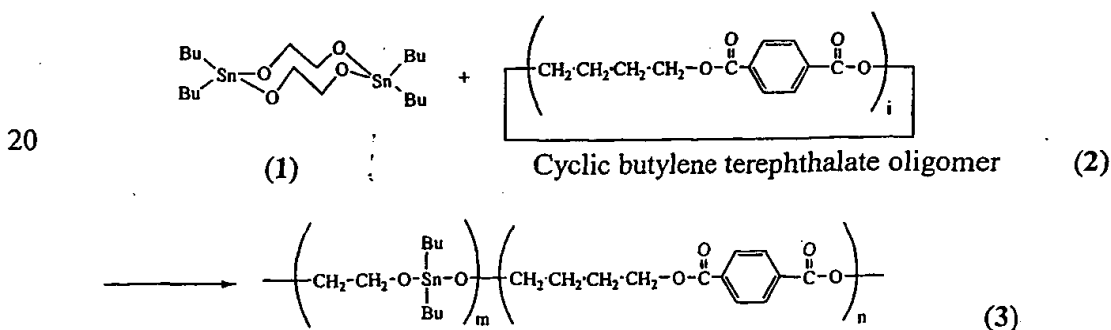
- 5 Organotin esters may be cyclic or acyclic. In some embodiments, the organotin esters that have the following formula (IV):



(IV)

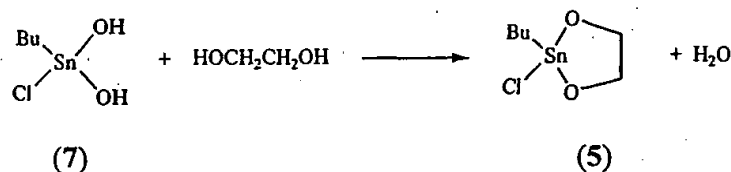
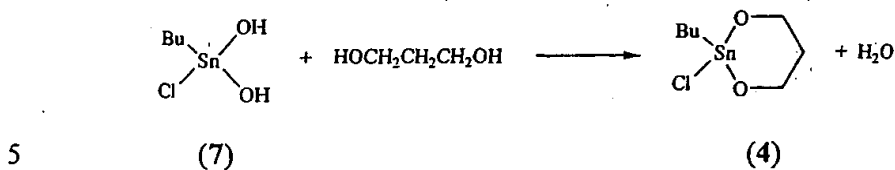
- where each of  $\text{R}_1$  and  $\text{R}_2$  independently is a halogen atom or an alkyl group; and each of  $\text{R}_3$  and  $\text{R}_4$  independently is a hydrogen atom or an alkyl group; or  $\text{R}_3-\text{O}$  and  $\text{R}_4-\text{O}$  taken together is an oxygen atom, or  $\text{R}_3$  and  $\text{R}_4$  taken together form a cyclic group. A cyclic group herein refers to any cyclic molecular group.

- [0060] For example, each of  $\text{R}_1$  and  $\text{R}_2$  independently is a halogen atom, a methyl group, an ethyl group, a propyl group, a butyl group.  $\text{R}_3-\text{O}$  and  $\text{R}_4-\text{O}$  taken together may be an oxygen atom such that the molecular structure becomes  $\text{R}_1-\text{Sn}(=\text{O})-\text{R}_2$ . Additionally,  $\text{R}_3$  and  $\text{R}_4$  taken together may form a cyclic structure such as a five- or six-membered ring with an oxygen atom and a tin atom as part of the ring. For example, 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (1) can polymerize with a macrocyclic butylene terephthalate oligoester (2) to give a copolyester (3) as shown below.

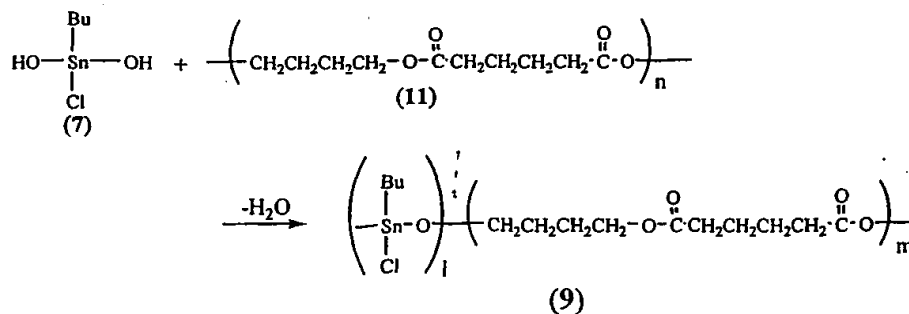
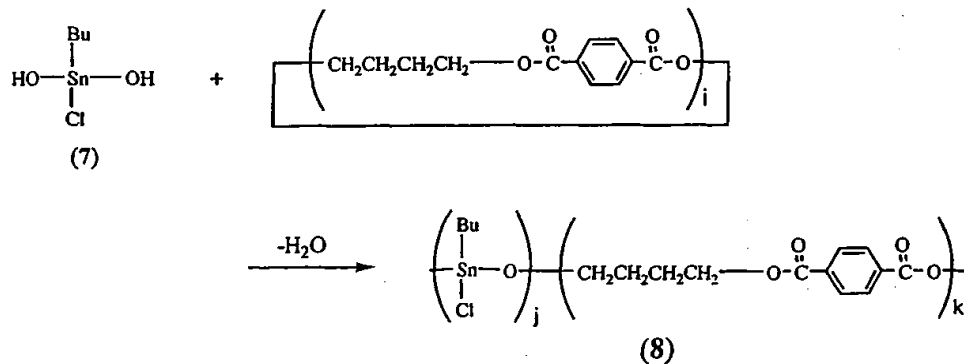


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[0061] In addition, organotin compounds such as (4) and (5) can react with oligoesters to form a copolyester. As shown below, compounds (4) and (5) are readily prepared from the diacid (7) and the appropriate diols.

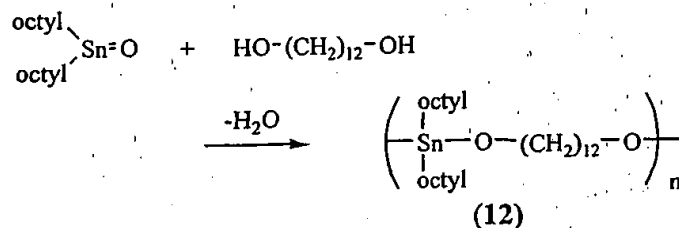
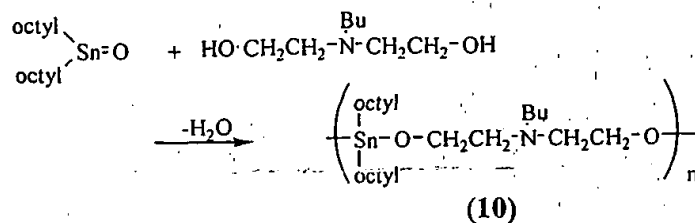


10 [0062] Organotin compounds having two hydroxyl groups can also dehydrate and polymerize with macrocyclic oligoesters to produce stannate copolyesters as shown below.



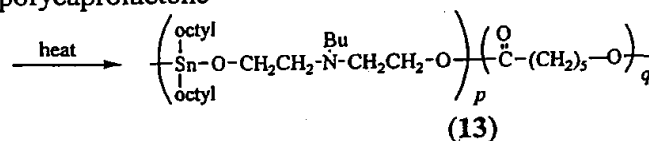
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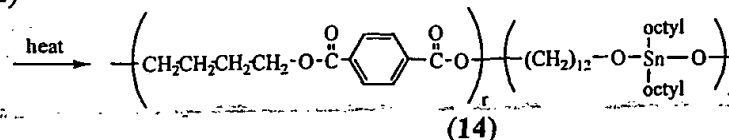


[0063] The polystannate esters (e.g., compounds (10) and (12)) may be incorporated into various poly(carboxy ester)s via a self-catalyzed ester interchange reaction to form organotin-containing copolyesters such as copolyesters 13, 14 and 15.

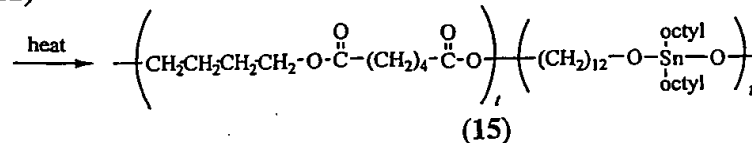
(10) + polycaprolactone



(12) + (2)



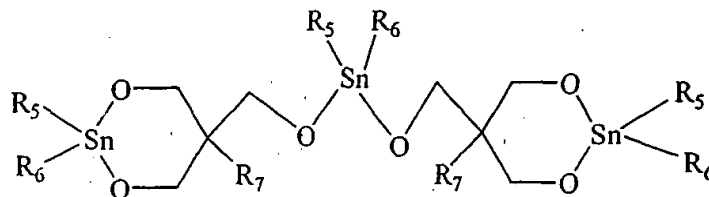
(12) + (11)



[0064] The organotin-containing copolyester products are useful ester-interchange polymerization catalysts for the production of high molecular weight polyesters.

[0065] In other embodiments, cyclic organotin esters that are useful in practice have the formula (V):

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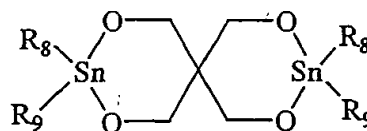


(V)

where each of  $R_5$  and  $R_6$  independently is C1-C10 alkyl group, and  $R_7$  is a C1-C4 primary alkyl group. For example,  $R_7$  may be a methyl group, an ethyl group, a primary propyl or butyl group.

- 5 Each of  $R_5$  and  $R_6$  may be a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, or an octyl group.

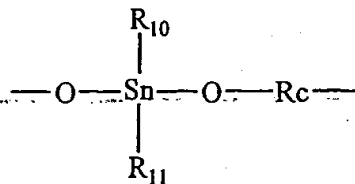
[0066] In yet other embodiments, cyclic organotin esters that may be employed have the formula (VI):



(VI)

- 10 where each of  $R_8$  and  $R_9$  independently is a C1-C10 alkyl group. Each of  $R_8$  and  $R_9$  may be a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group.

[0067] In yet other embodiments, organotin esters that are employed include an organotin ester polymer having the structural repeat unit of formula (VII)



(VII)

- 15 where each of  $R_{10}$  and  $R_{11}$  is C1-C10 alkyl group and  $R_c$  is C4-C20 alkylene radical.

[0068] Some of the organotin compounds and their analogues and homologues discussed herein are disclosed in the following commonly assigned patents, which are hereby incorporated by reference herein in their entirety: U.S. Patent Nos. 5,348,985; 5,386,037; 5,387,666; 5,389,719; and 5,466,744.

- 20 [0069] Oligoesters that may be employed include macrocyclic oligoesters, linear or branched oligoesters, and polyesters of various molecular weight. In one embodiment, the oligoester employed is a macrocyclic oligoester. In another embodiment, the oligoester employed is linear.

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In yet another embodiment, the oligoester employed is branched. In yet another embodiment, the oligoester employed is a polyester. In some embodiments, the organotin compound is a cyclic organotin ester. In other embodiments, the oligoester is a macrocyclic oligoester, and the organotin compound is a cyclic organotin ester. In yet other embodiments, the oligoester is not a macrocyclic oligoester, and the organotin compound is not a cyclic organotin ester. For example,

5 the oligoester may be a linear oligoester, and the organotin compound is a linear organotin ester. [0070] Catalysts may also be employed in the copolymerization of oligoesters and organotin compounds. Catalyst may not be needed because many organotin compounds themselves can serve as transesterification catalysts. However, catalysts may be employed in applications where

10 the organotin compound employed does not exhibit the desired reactivity, and/or a faster reaction is desired. As discussed above, organotin and organotitanate compounds are the preferred catalysts, although other catalysts may be used.

[0071] The polymerization reactions between oligoesters and organotin compounds are carried out at elevated temperatures. In one embodiment, the temperature is maintained within a range

15 from about 100°C to about 300°C. In another embodiment, the temperature is maintained within a range from about 100°C to about 190°C. In another embodiment, the temperature is maintained within a range from about 120°C to about 170°C. In yet another embodiment, the temperature is maintained within a range from about 140°C to about 170°C.

[0072] Non-metal-containing cyclic esters may be co-polymerized along with oligoesters and

20 organotin compounds. Non-metal-containing cyclic esters that may be employed include lactones. Lactones may be a cyclic ester of any membered ring. In one embodiment, lactones of 5-10 membered rings are used. The lactone can be unsubstituted or substituted. One or more carbon atoms in the lactone structure can be substituted with a heteroatom such as O, N, or S. One or more hydrogen atoms in the basic lactone structure can be substituted with a halogen

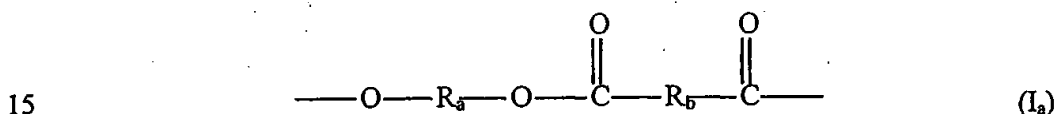
25 atom (e.g., F, Cl, Br, or I) or other functional groups including alkyl groups (e.g., methyl, ethyl, propyl, butyl, etc.), a hydroxyl group, alkyloxy groups, a cyano group, amino groups, and aromatic groups. The lactone can contain one or more additional rings. Illustrative examples of lactones include lactide, glycolide, dioxanone, 1,4-dioxane-2,3-dione,  $\epsilon$ -caprolactone,  $\beta$ -propiolactone, tetramethyl glycolide,  $\beta$ -butyrolactone,  $\gamma$ -butyrolactone, and pivalolactone.

**Macrocyclic Oligoesters**

[0073] One of the precursors employed in an embodiment of the invention to prepare copolyesters is an oligoester such as a macrocyclic oligoester. Oligoesters that may be employed  
 5 include alkylene dicarboxylate oligomers such as 1,4-butylene terephthalate oligomers and ethylene terephthalate oligomers. Depending on the desired properties of the final copolyester product, the appropriate oligoester(s) can be selected for use in its manufacture.

[0074] Many different macrocyclic oligoesters readily can be made and are useful in practice. Thus, depending on the desired properties of the final copolyester polymer product, the  
 10 appropriate macrocyclic oligoester(s) can be selected for use in its manufacture.

[0075] Macrocyclic oligoesters that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula (I<sub>a</sub>):

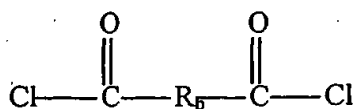


where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group.

[0076] Preferred macrocyclic oligoesters are macrocyclic oligoesters of ethylene terephthalate, propylene terephthalate, 1,3-propylene terephthalate, 1,4-butylene terephthalate, 1,4-  
 20 cyclohexylenedimethylene terephthalate, ethylene isophthalate, propylene isophthalate, 1,3-propylene isophthalate, 1,4-butylene isophthalate, 1,4-cyclohexylenedimethylene isophthalate, 1,2-ethylene 2,6-naphthalenedicarboxylate, and macrocyclic co-oligoesters thereof.

[0077] Synthesis of the macrocyclic oligoesters may be achieved by contacting at least one diol of the formula HO-R<sub>a</sub>-OH with at least one diacid chloride of the formula:

25



where R<sub>a</sub> and R<sub>b</sub> are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An  
 30 illustrative example of such amines is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible

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organic solvent such as methylene chloride. The temperature of the reaction typically is within the range of from about  $-25^{\circ}\text{C}$  to about  $25^{\circ}\text{C}$ . See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

5 [0078] Macrocyclic oligoesters also can be prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine. The condensation reaction is conducted in a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

10 [0079] Another method for preparing macrocyclic oligoesters or macrocyclic co-oligoesters is the depolymerization of linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to macrocyclic oligoesters by heating a mixture of linear polyesters, an organic solvent, and a transesterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are  
15 substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

[0080] It should be understood that it is within the scope of the invention to employ co-oligoesters (e.g., macrocyclic co-oligoesters) to produce copolyesters. Therefore, unless otherwise stated, a composition, article, or process that refers to oligoesters (e.g., macrocyclic  
20 oligoesters) also includes co-oligoesters (e.g., macrocyclic co-oligoesters).

#### Copolyesters Prepared from the Polymerization of Macrocyclic Oligoesters and Cyclic Esters

[0081] In another embodiment, the invention generally features a method of making a block  
25 copolymer of polyesters. Specifically, contacting a macrocyclic oligoester and a transesterification catalyst at an elevated temperature forms a first polymeric segment. Subsequently contacting the first polymeric segment, a cyclic ester that is not a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps are then sequentially repeated a desired number of times to  
30 form a block copolyester having additional first and second polymeric segments.

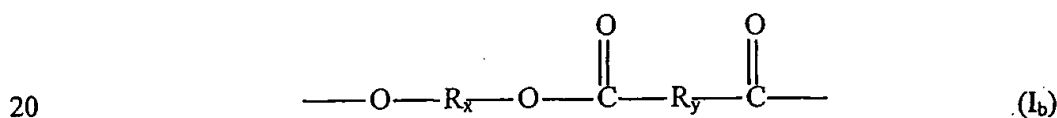
[0082] The above method of making a block copolymer may be modified in its sequence to begin with a cyclic ester. The polymerization may begin with a formation of a block of cyclic

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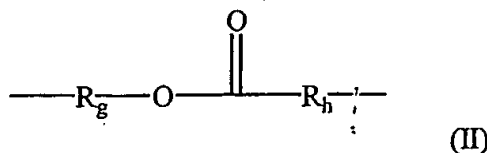
ester. Thus, a first polymeric segment is formed by contacting a cyclic ester that is not a macrocyclic oligoester and a transesterification catalyst at an elevated temperature. Subsequently contacting the first polymeric segment, a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps are then sequentially repeated a desired number of times to form a block copolymer having additional first and second polymeric segments.

[0083] In one embodiment, to prepare a block copolyester having blocks derived from a macrocyclic oligoester and a cyclic ester, the macrocyclic oligoester and the cyclic ester are reacted sequentially instead of simultaneously. Depending on the applications, it may be desirable to have a block copolymer having blocks derived from both macrocyclic oligoester and cyclic ester. Thus, the method of making a block copolymer can include a step of contacting a cyclic ester and a macrocyclic oligoester in the presence of a polymerization catalyst to form a third type of block. A protocol can be designed to achieve the desired copolyester having two or more different blocks. In addition, the same or different polymerization catalysts may be used in forming the two or more different blocks in preparing a block copolyester. More than one catalyst may be employed in each of the polymerization steps.

[0084] In yet another aspect, the invention features a composition of a copolyester. In one embodiment, the copolyester has, within its polymeric backbone, at least one structural unit of formula (I<sub>b</sub>)



where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a divalent aromatic or alicyclic group; and at least one structural unit of formula (II)



where R<sub>g</sub> and R<sub>h</sub> are independently a divalent organic moiety with the proviso that R<sub>g</sub> is not O-R<sub>x</sub>- if R<sub>h</sub> is -R<sub>y</sub>-C(O)-. R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group. R<sub>y</sub> is a divalent aromatic or alicyclic group.

[0085] In another aspect, the invention features a block copolymer of polyesters. In one embodiment, the block copolymer contains at least a first block unit and a second block unit.

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The first block unit has, within its polymeric backbone, at least one first structural unit of formula (I<sub>b</sub>). The second block unit has, within its polymeric backbone, at least one second structural unit of formula (II).

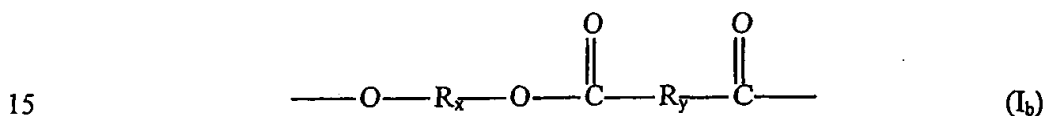
[0086] In one embodiment, the block copolymer contains additional blocks containing at least one structural unit of formula (I<sub>b</sub>) and containing at least one structural unit of formula (II).

Thus, a block copolymer may contain blocks derived from macrocyclic oligoesters, blocks derived from cyclic esters, and blocks derived from both macrocyclic oligoesters and cyclic esters. The length of the individual blocks and the sequence thereof can be designed to serve particular applications.

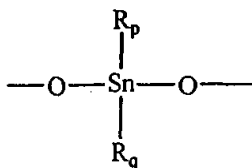
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#### Copolymers Prepared from the Polymerization of Macrocyclic oligoesters and Organotin Compounds

[0087] In yet another aspect, the invention features a copolyester. In one embodiment, the copolyester includes, within its polymeric backbone, (a) at least one structural unit of formula (I<sub>b</sub>)



where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a divalent aromatic or alicyclic group; and (b) at least one structural unit of formula (III)



(III)

where each of R<sub>p</sub> and R<sub>q</sub> independently is a halogen atom or an alkyl group.

[0088] In some embodiments, R<sub>x</sub> is one of an ethylene group and a 1,4-butylene group, and R<sub>y</sub> is a divalent benzene group. In other embodiments, each of R<sub>1</sub> and R<sub>2</sub> is a chlorine atom or a butyl group.

[0089] In some embodiments, the molar ratio of structural units of formula (I<sub>b</sub>) to structural units of formula (III) is from about 500:1 to about 0.5:1. In other embodiments, the molar ratio is from about 100:1 to about 0.5:1. In yet other embodiments, the molar ratio is from about 50:1 to about 1:1. In yet other embodiments, the molar ratio is from about 10:1 to about 1:1.

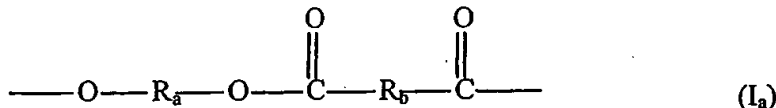
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[0090] The weight average molecular weights of the copolyesters typically are from about 1,000 to about 200,000. In one embodiment, the copolyester has a weight average molecular weight from about 1,000 to about 150,000. In another embodiment, the copolyester has a weight average molecular weight from about 1,000 to about 100,000. In yet another embodiment, the copolyester has a weight average molecular weight from about 1,000 to about 50,000. In yet another embodiment, the copolyester has a weight average molecular weight from about 10,000 to about 20,000.

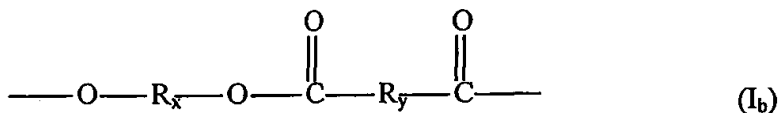
### Copolyesters as Polymerization Catalysts

[0091] In yet another aspect, the invention features a method for polymerizing a macrocyclic oligoester. In certain embodiments, tin-containing copolyesters disclosed above may be employed as transesterification catalysts in the polymerization of macrocyclic oligoesters. The method includes the steps of providing a macrocyclic oligoester, providing a polymerization catalyst, and contacting the macrocyclic oligoester and the polymerization catalyst at an elevated temperature thereby producing a copolyester. The macrocyclic oligoester has a structural repeat unit of formula (I<sub>a</sub>):

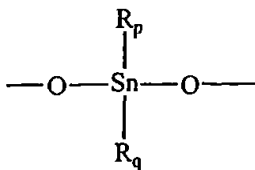


where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group. The polymerization catalyst includes at least one

component compound each of which has a formula that includes (i) at least one structural unit of formula (I<sub>b</sub>):



where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a divalent aromatic or alicyclic group; and (ii) at least one structural unit of formula (III)



(III)

where each of R<sub>p</sub> and R<sub>q</sub> independently is a halogen atom or an alkyl group.

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[0092] In some embodiments,  $R_x$  is one of an ethylene group and a 1,4-butylene group,  $R_y$  is a divalent benzene group, and each of  $R_1$  and  $R_2$  is a chlorine atom or a butyl group. In one embodiment, the molar ratio of structural units of formula (I<sub>b</sub>) to structural units of formula (III) is from about 500:1 to about 0.5:1. In another embodiment, the molar ratio is from about 100:1 to about 0.5:1. In yet another embodiment, the molar ratio is from about 50:1 to about 1:1. In yet another embodiment, the molar ratio is from about 10:1 to about 1:1.

[0093] The polymerization catalyst may include at least two component compounds that have a weight average molecular weight of from about 1,000 to about 200,000. In one embodiment, the copolyesters have a weight average molecular weight from about 1,000 to about 150,000. In another embodiment, the copolyesters have a weight average molecular weight from about 2,000 to about 120,000. In yet another embodiment, the copolyesters have a weight average molecular weight from about 2,000 to about 50,000. In yet another embodiment, the copolyesters have a weight average molecular weight from about 50,000 to about 120,000.

[0094] The polymerization typically is completed within about a few minutes to about a hour. The duration of the polymerization reaction depends on many factors such as the molar ratio of macrocyclic oligoester to the organotin copolyester catalyst, the temperature at which the polymerization reaction is carried out, the desired molecular weight, and the choice of solvent. The polymerization is preferably conducted under an inert environment, such as under nitrogen or argon, or under a vacuum.

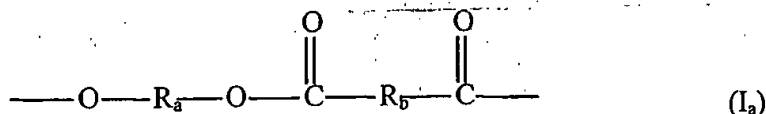
[0095] The polymerization reaction is carried out at an elevated temperature. In one embodiment, the temperature is maintained within a range from about 100°C to about 300°C. In another embodiment, the temperature is maintained within a range from about 100°C to about 190°C. In another embodiment, the temperature is maintained within a range from about 120°C to about 170°C. In yet another embodiment, the temperature is maintained within a range from about 140°C to about 170°C.

#### Mixtures of Macrocyclic Oligoesters And Catalysts

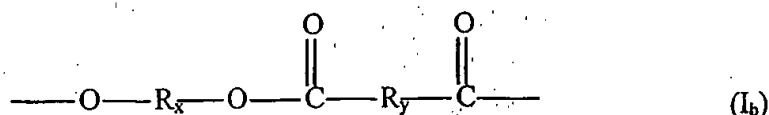
[0096] In yet another aspect, the invention features a method for manufacturing a mixture of a macrocyclic oligoester and a polymerization catalyst. The mixture is substantially free from water. The method includes the steps of mixing an oligoester with an organotin compound, heating the mixture of the oligoester and the organotin compound to an elevated temperature; removing water generated during the heating step, thereby obtaining a dried reaction mixture of

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oligoester and organotin compound; and mixing the dried reaction mixture of oligoester and the organotin compound with the macrocyclic oligoester having a structural repeat unit of formula (I<sub>a</sub>):



- 5 where R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>b</sub> is a divalent aromatic or alicyclic group. The oligoester has a structural repeat unit of formula (I<sub>b</sub>):



where R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and R<sub>y</sub> is a divalent aromatic or alicyclic group.

- 10 [0097] In one embodiment, the oligoester is a macrocyclic oligoester. In one embodiment, the organotin compound is an organotin ester. In one such embodiment, the organotin ester is a cyclic organotin ester. In one such embodiment, the oligoester is a macrocyclic oligoester, and the organotin ester is a cyclic organotin ester.

- [0098] The oligoester (e.g., macrocyclic oligoester) and the polymerization catalyst (e.g., organotin ester) may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the macrocyclic polyester oligomer with the polymerization catalyst via agitation at temperatures below the melting temperature of the macrocyclic polyester oligomer. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

- 20 [0099] A solvent may also be employed to assist in the uniform mixing of the macrocyclic oligoester with the polymerization catalyst. Various solvents can be used, and there is no limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water. Illustrative examples of solvents that may be employed in the invention include methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

25 [00100] The mixture of the oligoester and the organotin compound is heated to an elevated temperature. In some embodiments, the mixture of the oligoester and the organotin ester is heated to a temperature from about 100°C to about 190°C. In other embodiments, the mixture of the oligoester and the organotin ester is heated to a temperature from about 120°C to about

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170°C. In yet other embodiments, the mixture is heated to a temperature from about 145°C to about 165°C. In yet other embodiments, the mixture is heated to a temperature from about 155°C to about 165°C. The temperature and the duration of heating step may be selected such that no substantial hydrolysis of the oligoester occurs.

5 [00101] Water may be generated from the heating step and may be removed by any one of many means such as condensation of moisture through a condenser or pumping away under a reduced pressure. After the reaction mixture is dried, the reaction mixture of oligoester and organotin ester is mixed with a macrocyclic oligoester to produce a mixture of a macrocyclic oligoester and a polymerization catalyst.

10 [00102] In some embodiments, the molar ratio of the oligoester to the organotin ester mixed is from about 500:1 to about 0.5:1. In other embodiments, the molar ratio is from about 100:1 to about 0.5:1. In yet other embodiments, the molar ratio is from about 50:1 to about 1:1. In yet other embodiments, the molar ratio is from about 10:1 to about 1:1.

[00103] The mixture of macrocyclic oligoester and polymerization catalyst is substantially free  
15 from water. Substantially free from water means that the mixture has a water content less than about 2%. In one embodiment, the water content is less than about 0.5%. In yet another embodiment, the water content is less than about 2,000 ppm. In yet another embodiment, the water content is less than about 1,000 ppm. In yet another embodiment, the water content is less than about 500 ppm. In yet another embodiment, the water content is less than about 200 ppm.

20 [00104] In preferred embodiments, these methods of producing a mixture of a macrocyclic oligoester and a polymerization catalyst avoid exposing the bulk of the macrocyclic oligoester to water. By mixing the bulk of the macrocyclic oligoester (e.g., with organotin esters) after removal of water, only small portion of the macrocyclic oligoester is exposed to water. Hydrolysis of macrocyclic oligoester is therefore minimized.

25 [00105] Further, the reaction mixture of the organotin compound and the oligoester is an active catalyst. The tin content of the mixture may be controlled to allow easy mixing of the dried reaction mixture with the macrocyclic oligoester.

[00106] The compositions and methods of the invention may be used to manufacture articles of various size and shape from various macrocyclic oligoesters, organotin compounds, and cyclic  
30 esters. Exemplary articles that may be manufactured by the invention include without limitation automotive body panels and chassis components, bumper beams, aircraft wing skins, windmill

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blades, fluid storage tanks, tractor fenders, tennis rackets, golf shafts, windsurfing masts, toys, rods, tubes, bars stock, bicycle forks, and machine housings.

[00107] In the manufacture of an article, various types of fillers may be included. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silicate, titanium dioxide, calcium carbonate, chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers. A filler may be added before, during, or after the polymerization reaction between a macrocyclic oligoester and a cyclic ester. Fillers can be used to prepare polyester polymer composites.

[00108] Furthermore, in the manufacture of an article additional components (e.g., additives) may be added. Illustrative additives include colorants, pigments, magnetic materials, anti-oxidants, UV stabilizers, plasticizers, fire-retardants, lubricants, and mold releases.

### Examples

[00109] The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention. The products obtained from these examples may be confirmed by conventional techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, mass spectroscopy, infrared spectroscopy, differential scanning calorimetry and gel permeation chromatography analyses.

#### **Example A**

[00110] The macrocyclic oligoesters used in the following examples are the macrocyclic oligoesters of 1,4-butylene terephthalate. The macrocyclic oligoesters were prepared by heating a mixture of polyester linears, organic solvents, such as *o*-xylene and *o*-dichlorobenzene, which are substantially free of oxygen and water, and tin or titanium compounds as transesterification catalysts. See U.S. Patent No. 5,668,186 (incorporated herein by reference in its entirety).

**Example 1**

- [00111] A small vial (21 x 70 mm, 4 drum), equipped with a 2.5 cm magnetic stirring bar and an argon/vacuum adapter, was charged with 2.0 g of macrocyclic oligoesters of 1,4-butylene terephthalate. The vial was then connected to vacuum and immersed into an oil bath at 190°C. Upon melting, the molten liquid was dried for 3 minutes under 1 mm vacuum. The vacuum was then released with argon. Under argon, predetermined amount (51.9 mg to 415 mg) of  $\epsilon$ -caprolactone (dried over molecular sieves) was added via a syringe. The mixture was stirred for one minute at 190°C under argon. A predetermined amount (0.30 mole %) of tin catalyst Fomrez® SUL-11A was then added as a solution in *o*-dichlorobenzene. Fomrez® SUL-11A is a 1:1 reaction product of dibutyltin dioxide/DIOP plasticizer available from Witco Chemicals (Crompton Corporation). The resulting reaction mixture became viscous. Stirring stopped within about 5 to 10 seconds. After 15 minutes, the vial was removed from the oil bath and was immediately cooled with ice-water. The vial was broken to retrieve a sample of the polymer. After dissolution in 15% hexfluoroisopropanol/chloroform, the sample was analyzed by gel permeation chromatography (GPC). The test results are shown in Table 1.

**Table 1. Co-Polymerization Of Macrocyclic Oligoesters CBT With  $\epsilon$ -Caprolactone Using A Tin Catalyst**

$\epsilon$ -Caprolactone/CBT (Molar Ratio)	% Polymer	Mw <sup>a</sup>	T <sub>m</sub> (°C) <sup>b</sup>	Temp. Range Of Melting Endotherm (°C)	$\Delta H^c$ (J/g)
00/100	94	132,300	221	198-230	49.7
05/100	96	140,180	214	200 - 220	43.9
15/100	96	139,680	196	175 - 220	23.1
20/100	98	121,850	190	175 - 220	24.7
25/100	97	134,490	185	160 - 220	19.8
30/100	97	130,400	177	160 - 190	17.8
35/100	98	128,800	170	150 - 180	14.4
40/100	92	136,000	164	145 - 180	11.8

<sup>a</sup> Molecular weight (by GPC relative to polystyrene standards)

<sup>b</sup> Peak temperature of the melting endotherm (by DSC with heating rate of 20°C/min)

<sup>c</sup> Heat of melting (DSC with a heating rate of 20°C/min)

**Example 2**

- [00112] A small vial (21 x 70 mm, 4 drum), equipped with a 2.5 cm magnetic stirring bar and argon/vacuum adapter, was charged with 2.0 g of macrocyclic oligoesters of 1,4-butylene

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terephthalate. The vial was then connected to vacuum and immersed into an oil bath at 190°C. Upon melting, the molten liquid was dried for 3 minutes under 1 mm vacuum. The vacuum was then released with argon. Under argon, predetermined amount (51.9 mg to 415 mg) of  $\epsilon$ -caprolactone (dried over molecular sieves) was added via a syringe. The mixture was stirred for one minute at 190°C under argon. A predetermined amount (0.30 mole %) of titanate catalyst Tyzor® TPT was then added as a solution in *o*-dichlorobenzene. Tyzor® TPT is tetra-isopropyl titanate available from E.I. du Pont Nemours and Company (Wilmington, Delaware). The resulting reaction mixture became viscous. Stirring stopped within about 5 to 10 seconds. After 15 minutes, the vial was removed from oil bath, and was immediately cooled with ice-water. The vial was then broken to retrieve a sample of the polymer. After dissolution in 15% hexfluoroisopropanol/chloroform, the sample was analyzed by GPC. The test results are shown in Table 2.

**Table 2. Co-Polymerization Of Macrocyclic Oligoesters CBT  
With  $\epsilon$ -Caprolactone Using A Titanate Catalyst**

$\epsilon$ -Caprolactone/CBT (Molar Ratio)	% Polymer	Mw <sup>a</sup>	Tm (°C) <sup>b</sup>	Temp. Range Of Melting Endotherm (°C)	$\Delta H^c$ (J/g)
25/100	98%	95,000	190	170-200	13.0

<sup>a</sup> Molecular weight (by GPC relative to polystyrene standards)

<sup>b</sup> Peak temperature of the melting endotherm (by DSC with heating rate of 20°C/min)

<sup>c</sup> Heat of melting (by DSC with heating rate of 20°C/min)

### Examples 3

[00113] A 100 mL 3-necked flask is charged with 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (0.733g, 0.0025 mol tin; 10 mol%), macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (4.923g, 0.0225 mol repeat unit; 90 mol%), and 20 mL of dry *o*-dichlorobenzene. The mixture (a solution) was stirred under nitrogen blanket and was heated in an oil bath. The viscosity of the mixture started to increase when the temperature rose to about 160°C. On heating at about 170°C for 15 minutes, the mixture became very viscous. Further heating at about 170°C for additional 60 minutes was followed by cooling the mixture. When the mixture was cooled to about 130°C precipitation (due to polymer formation) started to occur. The mixture was diluted with 20 mL of toluene and cooled to room temperature. The precipitate was filtered, washed with toluene and dried under vacuum at 60°C. The yield of the polymer, a white powder, was

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5.08g or 90%. GPC analysis revealed that conversion of macrocyclic oligoester was 100% and the peak molecular weight was 47,000 daltons.

#### Example 4

5 [00114] A 100 mL 3-necked flask is charged with 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (1.465g, 0.005 mol tin; 20 mol%), macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (4.376g, 0.020 mol repeat unit; 80 mol%), and 20 mL of dry *o*-dichlorobenzene. The mixture (a solution) was stirred under nitrogen blanket and was heated in an oil bath. The viscosity of the mixture  
10 started to increase when the temperature rose to about 160°C. On heating at about 170°C for 15 min, the mixture became very viscous. Further heating at about 170°C for additional 60 minutes was followed by cooling the mixture. When the mixture was cooled to about 130°C precipitation (due to polymer formation) started to occur. The mixture was diluted with 20 mL of toluene and cooled to room temperature. The precipitate was filtered, washed with toluene and dried under  
15 vacuum at 60°C. The yield of the polymer, a white powder, was 5.33g or 91%. GPC analysis revealed that conversion of macrocyclic oligoester was 94% and the peak molecular weight was 43,000 daltons.

#### Example 5

20 [00115] A 100 mL 3-necked flask is charged with 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (1.465g, 0.005 mol; 20 mol%), macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (0.875g, 0.004 mol; 16 mol%),  $\epsilon$ -caprolactone (1.826g, 0.016 mol; 64 mol%), and 20 mL of dry *o*-dichlorobenzene. The mixture (a solution) was stirred under nitrogen blanket and was heated in  
25 an oil bath. The viscosity of the mixture started to increase when the temperature rose to about 160°C. On heating at about 170°C for 15 minutes, the mixture became very viscous. Further heating at about 170°C for additional 60 min was followed by cooling the mixture. When the mixture was cooled to about 130°C precipitation (due to polymer formation) started to occur. The mixture was diluted with 20 mL of hexane and cooled to room temperature. The precipitate  
30 was filtered, washed with hexane and dried under vacuum at 60°C. GPC analysis revealed that the peak molecular weight was 19,000 daltons.

**Example 6**

[00116] A 100 mL 3-necked flask is charged with 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (1.465g, 0.005 mol; 10 mol%), macrocyclic oligoester composed of 95  
5 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (4.923g, 0.0225 mol; 45 mol%),  $\epsilon$ -caprolactone (2.568g, 0.0225 mol; 45 mol%), and 20 mL of dry *o*-dichlorobenzene. The mixture (a solution) was stirred under nitrogen blanket and was heated in an oil bath. The viscosity of the mixture started to increase when the temperature rose to about 160°C. On heating at about 170°C for 15 minutes, the mixture became very viscous. Further  
10 heating at about 170°C for additional 60 minutes was followed by cooling the mixture. When the mixture was cooled to about 130°C precipitation (due to polymer formation) started to occur. The mixture was diluted with 20 mL of hexane and cooled to room temperature. The precipitate was filtered, washed with hexane and dried under vacuum at 60°C. GPC analysis revealed that the peak molecular weight was 69,000 daltons.

15

**Example 7**

[00117] A 10 mL test tube is charged with a mixture of the tin copolyester powder prepared from Example 3 (0.093g, 0.041 mmol Sn) and macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol % ethylene terephthalate structural repeat units (3.00g, 13.71  
20 mmol). The mixture was dried at 100°C under vacuum for 30 minutes and was then heated at 190°C under nitrogen for 20 minutes. The resulting polymer had a conversion of 95%, GPC peak molecular weight of 256,000 daltons, and a weight average molecular weight of 339,000 daltons.

**Example 8**

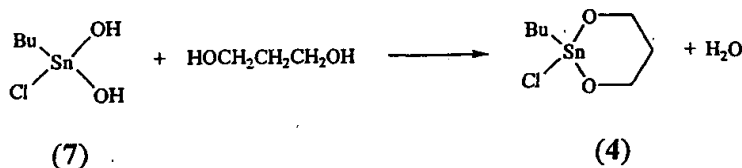
[00118] A 10 mL test tube is charged with 0.3 g of a mixture of the tin copolyester powder prepared from Example 4 (0.016g, 0.0137 mmol Sn) and macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol % ethylene terephthalate structural repeat units (1.00g, 4.44 mmol). The mixture was dried at about 100°C under vacuum for about 30 minutes and was  
30 then heated at about 190°C under nitrogen for about 20 minutes. The resulting polymer had a GPC peak molecular weight of 151,000.

**Example 9**

[00119] Tin copolyester obtained in Example 5 (0.018 g, 0.0216 mmol Sn) was dissolved in toluene (1.5 mL). The toluene solution was combined with macrocyclic oligoester composed of  
 5 95 mol% butylene terephthalate and 5 mol % ethylene terephthalate structural repeat units (1.58 g, 72.0 mmol). The resulting paste was dried under vacuum and pulverized. Approximately 0.3 g of the mixture was placed in a 10 mL test tube. Polymerization was conducted at about 190°C for about 20 minutes. The polymer had a GPC peak molecular weight of 160,000 daltons.

**Example 10**

[00120] A 250 ml 3-neck flask equipped with a Dean-Stark condenser was charged with butyltin chloride dihydroxide (12.26 g, 0.05 mol), 1,3-propanediol (3.81g, 0.05 mol), and 50 mL of toluene. The mixture was heated to reflux, and water generated was removed over a period of about 3 hours. The Dean-Stark condenser was then replaced with a molecular sieve trap, and the  
 15 system was dried for additional 3 hours of reflux. The resulting clear reaction solution was evaporated under vacuum to obtain a glassy solid having the following formula (4). The yield was 13.6 g or 95%%.

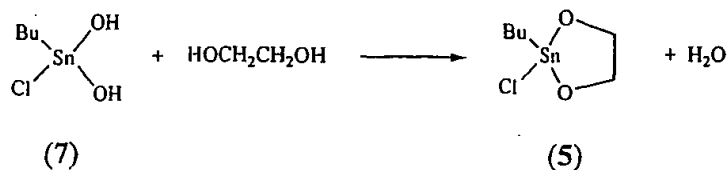


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**Example 11**

[00121] A 250 ml 3-neck flask equipped with a Dean-Stark condenser was charged with butyltin chloride dihydroxide (12.26 g, 0.05 mol), ethylene glycol (3.10 g, 0.05 mol), and 40 mL of toluene. The mixture was heated to reflux, and water generated was removed over a period of  
 25 about 3 hours. The Dean-Stark condenser was then replaced with a molecular sieve trap, and the system was dried for additional 1.5 hours of reflux. The resulting clear reaction solution was evaporated under vacuum to obtain a crystalline solid having the following formula (5), m.p.=138-141°C. The yield was 12.77g or 94%.

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**Example 12**

5 [00122] A 100 mL 3-neck flask was charged with the cyclic tin compound (4) from Example 10 (0.7134g, 2.5 mmol), macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol % ethylene terephthalate structural repeat units (4.923g, 22.5 mmol) and 10 mL of *o*-dichlorobenzene. The solution was stirred under nitrogen and was heated at about 180°C for about 15 minutes. The conversion of macrocyclic oligoester was 100%. GPC peak molecular weight was 15,000 daltons. The solution was further heated for a total of about 120 minutes. The copolymer was isolated by precipitation in pentane. The yield was 5.41g or 96%. GPC peak molecular weight was 14,000 daltons.

**Example 13**

15 [00123] A 100 mL 3-neck flask was charged with the cyclic tin compound (5) from Example 11 (0.678g, 2.5 mmol), macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol % ethylene terephthalate structural repeat units (4.923g, 22.5 mmol) and 10 mL of *o*-dichlorobenzene. The mixture was stirred under nitrogen and heated at about 170-175°C for one hour. The product was precipitated in toluene and isolated. The conversion of macrocyclic oligoester was 93%. The yield was 4.93g or 95%. The GPC peak molecular weight was 27,400 daltons.

**Example 14**

[00124] A 130 mL culture tube equipped with a vacuum adapter was charged with a powder of macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (10.00g, 45.45 mmol repeat units). The powder was dried under vacuum at about 100°C for 0.5 hour and melted by heating at about 160°C for about 12 minutes. A finely pulverized butyltin chloride dihydroxide (7; 0.67g, 2.73 mmol) was added with stirring to the above molten macrocyclic oligoester. Water that was generated was removed under vacuum. When the resulting intermediate product was further heated at about 190°C for about 20 minutes a white crystalline solid was obtained. The solid (a copolymer) had a weight average molecular weight of 39,100 daltons.

**Example 15**

[00125] A 50 mL culture tube equipped with a vacuum adapter was charged with finely pulverized poly(1,4-butylene adipate) (11; 3.00g, 13.6 mmol repeat units) and butyltin chloride dihydroxide (7; 0.372g, 1.51 mmol, 10 mol%). The mixture was dried under vacuum and was then heated at about 145°C for about 0.5 hour during which time water generated was removed under vacuum. Viscous clear material resulted which on cooling crystallized to form an opaque white solid. The yield of the product (a copolyester, 9) was 3.21 g or 96%. The copolymer contained 0.45 mmol/g of tin atoms. The DSC analysis of the copolyester showed a m.p. of 51.5°C.

**Example 16**

[00126] A finely pulverized powder of intermediate copolyester product described in Example 14 (0.268g, 0.069 mmol Sn) and macrocyclic oligoester composed of 95 mol% butylene terephthalate and 5 mol% ethylene terephthalate structural repeat units (5.09g, 2.32 mmol repeat units)) were intimately blended. A part of the blended mixture (0.3 g, 1.36 mmol repeat units) was then heated and polymerized at about 190°C. The resulting polyester showed conversion yields of 80.0% and 92.7 %, and weight average molecular weights of 104,800 daltons and 108,800 daltons, at reaction time of 20 and 40 minutes, respectively.

**Example 17**

[00127] A 30 mL culture tube fitted with a vacuum adapter was charged with a mixture of organotin copolyester prepared in Example 15 (9; 40 mg, 0.018 mmol Sn) and macrocyclic butylene terephthalate (1.45g, 6.57 mmol repeat units). The tube was heated under vacuum in an oil bath at about 165°C. The molten mixture was stirred magnetically for about 5 minutes. The clear molten mixture was then heated under nitrogen at about 190°C. The molten mixture polymerized and solidified within 10 minutes. After total heating time at 190°C of 40 minutes, the polymer was cooled and analyzed by GPC. The product showed a weight average molecular weight of 192,000 daltons and a conversion yield of 69%.

**Example 18**

[00128] A 30 mL culture tube fitted with a vacuum adapter was charged with dioctyltin oxide (3.79g, 10.5 mmol) and N-butyldiethanolamine (1.69g, 10.5 mmol). The tube was heated under vacuum in an oil bath at about 130°C for about 1.5 hours. The resulting clear viscous liquid was further heated at about 155°C for an additional hour and was allowed to cool. The yield of a waxy semisolid polymer was 5.22g or 98% with a melting peak of 76°C.

**Example 19**

[00129] A 30 mL culture tube fitted with a vacuum adapter was charged with a mixture of dioctyltin oxide (3.61g, 10 mmol) and 1,12-dodecanediol (2.02g, 10 mmol). The tube was heated under vacuum at about 130°C. The temperature was gradually raised 190°C over a period of 3 hours. The resulting viscous clear liquid was allowed to cool. The yield of the white crystalline polymer weighed 5.46g or 99% with a melting temperature of 80.4°C.

**Example 20**

[00130] A 30 mL culture tube fitted with a vacuum adapter was charged with the stannate polymer prepared in Example 18 (10; 0.403g, 0.80 mmol tin) and polycaprolactone (0.821g, 7.2 mmol repeat units). The tube was heated under vacuum at about 140°C and the temperature was gradually raised to about 175°C over a period of 15 minutes. Upon cooling, a white crystalline copolyester (10 mol% stannate) was obtained. The yield was 1.21g or 99% with a tin content of 0.65 mmol/g and a melting temperature of 45.8°C.

**Example 21**

[00131] A 30 mL culture tube fitted with a vacuum adapter was charged with the stannate polymer prepared in Example 19, poly(dodecane-1,12-diyl dioctylstannate) (12; 0.921g, 1.69 mmol repeat units) and macrocyclic oligoester composed of 95mol% butylene terephthalate and 5mol% ethylene phthalate units (1.485g, 6.75 mmol repeat units). The tube was heated under vacuum at about 150 °C, and the temperature was gradually increased to about 205°C over a period of 16 minutes. The product (a copolyester) was allowed to cool to room temperature. The yield of the white crystalline copolyester (20 mol% stannate) was 2.36g or 98% yield with a melting temperature of 188°C.

**Example 22**

[00132] A 30 mL culture tube fitted with a vacuum adapter was charged with the stannate polymer prepared in Example 19, poly(dodecane-1,12-diyl dioctylstannate) (12; 0.978g, 1.79 mmol repeat units) and poly(1,4-butylene adipate) (1.436g, 7.17 mmol repeat units). The tube was heated under vacuum at about 110°C. The molten mixture was gradually heated up to about 170°C over a period of 15 minutes, and the resulting viscous liquid was allowed to cool to room temperature. The yield of the waxy product (a copolyester) was 2.34g or 97% with a melting temperature of 34°C as measured by DSC.

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**Example 23**

[00133] The copolyester prepared in Example 20 (13; 0.052g, 0.034 mmol Tin) was dissolved in toluene (2 mL) placed in a 30 ml jar. The solution was combined with a fine powder of macrocyclic oligoester composed of butylene terephthalate structural repeat units (2.49g, 11.3 mmol repeat units), and the resulting white paste was dried under vacuum at 80°C. A portion of approximately 0.3g of the resulting one-part mixture was then subjected to test polymerization at about 190°C under nitrogen. The results are summarized in Table 3.

**Example 24**

[00134] A 30 mL jar was charged with the copolyester prepared in Example 21(14; 0.048 g, 0.0337 mmol Tin). Toluene (2.5 mL) was added to dissolve the copolyester. The solution was combined with a fine powder of macrocyclic oligoester composed of butylene terephthalate structural units 2.47 g, 11.2 mmol repeat units), and the resulting white paste was dried under vacuum at 80°C. A 0.3g portion of the resulting one-part mixture was then subjected to test polymerization at 190°C under nitrogen. The results are summarized in Table 3.

**Example 25**

[00135] A 30 mL glass jar was charged with the copolyester prepared in Example 22 (15; 0.089 g, 0.0688 mmol Tin). Toluene (4.5 mL) was added to dissolve the copolyester. The solution was combined with a fine powder of macrocyclic oligoester composed of butylene terephthalate structural repeat units (5.05 g, 22.9 mmol repeat units), and the resulting white paste was dried under vacuum at 80°C. A portion of the one-part mixture was then subjected to test polymerization at 190°C under nitrogen. The results are summarized in Table 3.

**Example 26**

[00136] A 30 mL glass jar was charged with the copolyester, poly(N-butyl-3-azapentane-1,5-diyl dioctylstannate), prepared in Example 18 (10; 17.1 mg, 0.0339 mmol Sn). Toluene (2 mL) was added to dissolve the copolyester. The solution was combined with a fine powder of macrocyclic oligoester composed of butylene terephthalate structural repeat units (2.48g, 11.3 mmol of repeat units). The resulting white paste was dried and pulverized. A portion of the one-part mixture was then test polymerized at 190 °C under nitrogen. The results are shown in Table 3.

**Example 27**

[00137] Copolyester, poly(dodecane-1,12-diyl dioctylstannate), prepared in Example 19 (12; 18.5mg, 0.0339 mmol Sn) was placed in a 30 ml jar and toluene (2 mL) was added to dissolve

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the copolyester. The solution was combined with a fine powder of macrocyclic oligoester, composed of butylene terephthalate structural repeat units (2.48g, 11.3 mmol of repeat units). The resulting white paste was dried and pulverized. A portion of the one-part mixture was then test polymerized at 190 °C under nitrogen. The results are shown in Table 3.

5

**Table 3. Polymerization of CBT with stannate copolyesters as catalyst**

Tin polymer catalysts <sup>a</sup>	Polymer conversion (%)			GPC peak M <sub>w</sub> (x 10 <sup>-3</sup> )		
	min at 190°C/N <sub>2</sub>			min at 190°C/N <sub>2</sub>		
	3	5	10	3	5	10
10	91.1	91.9	96.9	168.0	174.8	174.8
12	92.7	97.7	98.6	139.6	143.7	145.4
13	92.0	96.6	96.1	143.8	149.7	141.3
14	97.7	96.2	98.0	143.5	146.9	145.2
15	92.9	95.8	96.2	136.8	141.7	145.8

<sup>a</sup> - Used 0.3 mol% Sn-based on total butylene terephthalate units in macrocyclic oligoester.

10

[00138] Each of the patent documents disclosed hereinabove is incorporated by reference herein in their entirety. Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

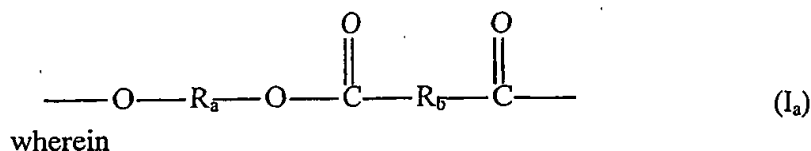
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## CLAIMS

What is claimed is:

- 1 1. A method of making a copolyester, the method comprising the steps of:
- 2 (a) providing a macrocyclic oligoester having a structural repeat unit of formula (I<sub>a</sub>):



- 5  $\text{R}_a$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;
- 6 and
- 7  $\text{R}_b$  is a divalent aromatic or alicyclic group;
- 8 (b) providing a cyclic ester, wherein the cyclic ester is not a macrocyclic oligoester;
- 9 and
- 10 (c) contacting the macrocyclic oligoester and the cyclic ester in the presence of a
- 11 transesterification catalyst at an elevated temperature to produce the copolyester.

1 2. The method of claim 1 wherein the cyclic ester is a lactone.

1 3. The method of claim 2 wherein the lactone is  $\epsilon$ -caprolactone.

1 4. The method of claim 1 wherein the macrocyclic oligoester comprises macrocyclic  
2 oligo(1,4-butylene terephthalate).

1 5. The method of claim 1 wherein the macrocyclic oligoester comprises macrocyclic  
2 oligo(ethylene terephthalate).

1 6. The method of claim 1 wherein the transesterification catalyst comprises a tin compound.

1 7. The method of claim 6 wherein the tin compound is a dialkyltin oxide.

1 8. The method of claim 1 wherein the transesterification catalyst comprises a titanate  
2 compound.

1 9. The method of claim 8 wherein the titanate compound is an alkyl titanate.

1 10. The method of claim 1 wherein the elevated temperature is within a temperature range  
2 from about 100°C to about 300°C.

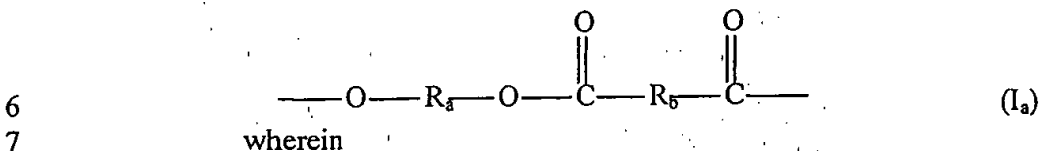
1 11. The method of claim 1 wherein the elevated temperature is within a temperature range  
2 from about 100°C to about 260°C.

1 12. The method of claim 1 wherein the elevated temperature is within a temperature range  
2 from about 150°C to about 210°C.

- 37 -

1 13. A method of making a block copolymer of polyesters, the method comprising the steps  
2 of:

3 (a) contacting a macrocyclic oligoester and a transesterification catalyst at an elevated  
4 temperature to form a first polymeric segment, wherein the macrocyclic oligoester  
5 has a structural repeat unit of formula (I<sub>a</sub>):



8 R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;  
9 and

10 R<sub>b</sub> is a divalent aromatic or alicyclic group;

11 (b) contacting a cyclic ester, the first polymeric segment, and the transesterification  
12 catalyst at an elevated temperature to form a second polymeric segment, wherein  
13 the cyclic ester is not a macrocyclic oligoester; and

14 (c) sequentially repeating steps (a) and (b) a desired number of times to form a block  
15 copolymer having additional first and second polymeric segments.

1 14. The method of claim 13 wherein the cyclic ester is a lactone.

1 15. The method of claim 13 wherein the macrocyclic oligoester is macrocyclic oligo(1,4-  
2 butylene terephthalate).

1 16. The method of claim 13 wherein the transesterification catalyst comprises a tin  
2 compound.

1 17. The method of claim 13 wherein the transesterification catalyst comprises a titanate  
2 compound.

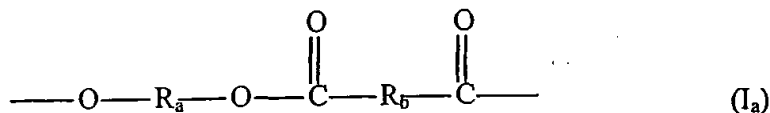
1 18. The method of claim 13 wherein the elevated temperature is within a temperature range  
2 from about 100°C to about 300°C.

1 19. A method of making a block copolymer of polyesters, the method comprising the steps  
2 of:

3 (a) contacting a cyclic ester and a transesterification catalyst at an elevated  
4 temperature to form a first polymeric segment, wherein the cyclic ester is not a  
5 macrocyclic oligoester; and

- 38 -

- (b) contacting a macrocyclic oligoester, the first polymeric segment, and the transesterification catalyst at an elevated temperature to form a second polymeric segment, wherein the macrocyclic oligoester has a structural unit of formula (I<sub>a</sub>)



wherein

R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

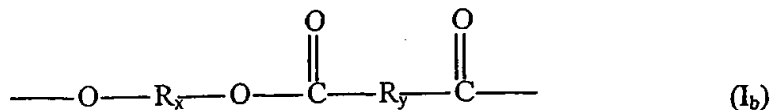
and

R<sub>b</sub> is a divalent aromatic or alicyclic group; and

- (c) sequentially repeating steps (a) and (b) a desired number of times to form a block copolymer having additional first and second polymeric segments.

20. A copolyester comprising, within its polymeric backbone,

- (a) at least one structural unit of formula (I<sub>b</sub>)



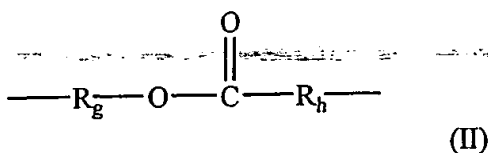
wherein

R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

R<sub>y</sub> is a divalent aromatic or alicyclic group; and

- (b) at least one structural unit of formula (II)



wherein

R<sub>g</sub> and R<sub>h</sub> are independently a divalent organic moiety with the proviso that R<sub>g</sub> is not -O-R<sub>x</sub>- if R<sub>h</sub> is -R<sub>y</sub>-C(O)-

wherein

R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

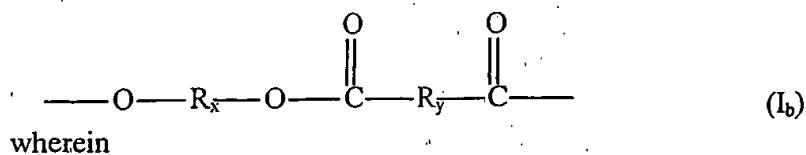
R<sub>y</sub> is a divalent aromatic or alicyclic group.

21. The copolyester of claim 20 wherein R<sub>x</sub> is 1,4-butylene and R<sub>y</sub> is benzene.

1 22. The copolyester of claim 20 wherein  $R_x$  is ethylene and  $R_y$  is benzene.

1 23. A block copolymer comprising

2 (a) a first block unit comprising, within its polymeric backbone, at least one structural  
3 unit of formula (I<sub>b</sub>)

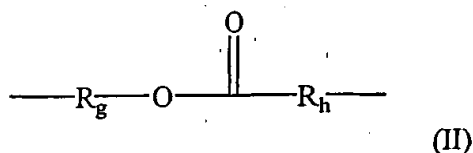


6  $R_x$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

7 and

8  $R_y$  is a divalent aromatic or alicyclic group; and

9 (b) a second block unit comprising, within its polymeric backbone, at least one  
10 structural unit of formula (II)



12 wherein

13  $R_g$  and  $R_h$  are independently a divalent organic moiety with the proviso

14 that  $R_g$  is not  $\text{---O---}R_x\text{---}$  if  $R_h$  is  $\text{---}R_y\text{---C(O)---}$

15 wherein

16  $R_x$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

17 and

18  $R_y$  is a divalent aromatic or alicyclic group.

1 24. A copolyester prepared by the method of claim 1.

1 25. A block copolymer of polyesters prepared by the method of claim 14.

1 26. A block copolymer of polyesters prepared by the method of claim 19.

1 27. An article of manufacture comprising the copolyester of claim 20.

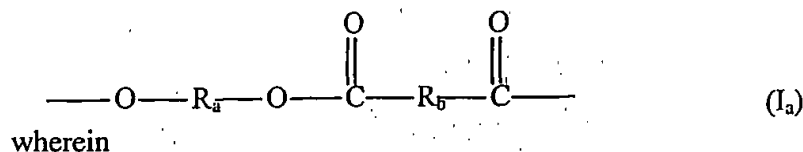
1 28. A composite material comprising the block copolymer of claim 23.

1 29. An article of manufacture comprising the block copolymer of claim 23.

2 30. A method for making an organotin copolyester, the method comprising the steps of:

3 (a) providing an oligoester having a structural repeat unit of formula (I<sub>a</sub>):

- 40 -



$R_a$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

$R_b$  is a divalent aromatic or alicyclic group;

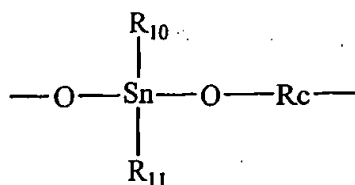
(b) providing a non-catalytic amount of an organotin compound; and

(c) contacting the oligoester and the organotin compound at an elevated temperature to produce an organotin copolyester.

31. The method of claim 30 wherein the oligoester is a macrocyclic oligoester.

32. The method of claim 30 wherein the organotin compound is an organotin ester.

33. The method of claim 32 wherein the organotin ester is an organotin ester polymer having a structural repeat unit of formula (VII)



(VII)

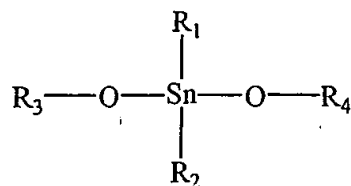
where each of  $R_{10}$  and  $R_{11}$  is C1-C10 alkyl group and  $R_c$  is C4-C20 alkylene group.

34. The method of claim 32 wherein the organotin ester is a cyclic organotin ester.

35. The method of claim 30 wherein the oligoester is a macrocyclic oligoester and the organotin compound is a cyclic organotin ester.

36. The method of claim 31 wherein the macrocyclic oligoester are selected from the group consisting of macrocyclic oligoesters of ethylene terephthalate, propylene terephthalate, 1,3-propylene terephthalate, 1,4-butyleneterephthalate, 1,4-cyclohexylenedimethyleneterephthalate, ethylene isophthalate, propylene isophthalate, 1,3-propylene isophthalate, 1,4-butylenisophthalate, 1,4-cyclohexylenedimethylenisophthalate, 1,2-ethylene 2,6-naphthalenedicarboxylate, and macrocyclic co-oligoesters thereof.

37. The method of claim 30 wherein the cyclic organotin compound has the formula (IV)



(IV)

wherein

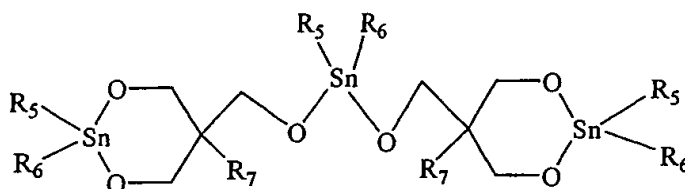
each of  $R_1$  and  $R_2$  independently is a halogen atom or an alkyl group, and

each of  $R_3$  and  $R_4$  independently is a hydrogen atom or an alkyl group, or  $R_3$  and

$R_4$  taken together form a cyclic group; or  $R_3-O$  and  $R_4-O$  taken together is an

oxygen atom.

38. The method of claim 32 wherein the cyclic organotin ester has the formula (V)

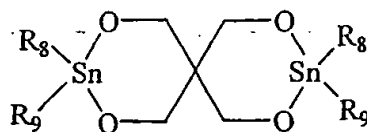


(V)

wherein  $R_7$  is a C1-C4 primary alkyl group and  $R_5$  and  $R_6$  is C1-C10 alkyl group.

39. The method of claim 38 wherein  $R_7$  is a methyl group and each of  $R_5$  and  $R_6$  is a butyl group.

40. The method of claim 32 wherein the cyclic organotin ester has the formula (VI)

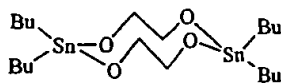


(VI)

wherein each of  $R_8$  and  $R_9$  is a C1-C10 alkyl group.

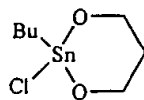
41. The method of claim 40 wherein each of  $R_8$  and  $R_9$  is a butyl group.

42. The method of claim 35 wherein the macrocyclic oligoester comprises macrocyclic oligo(1,4-butylene terephthalate) and the cyclic organotin ester is selected from the group consisting of a compound having the formula of (VIII),



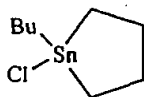
(VIII)

a compound having the formula of (IX),



(IX)

and a compound having the formula of (X)



(X).

43. The method of claim 30 comprising the step of providing a non-metal-containing cyclic ester, wherein step (c) comprising contacting the oligoester, the organotin ester, and the non-metal-containing cyclic ester at an elevated temperature to produce an organotin copolyester.

44. The method of claim 43 wherein the non-metal-containing cyclic ester is a lactone.

45. The method of claim 43 wherein the non-metal-containing cyclic ester is  $\epsilon$ -caprolactone.

46. The method of claim 30 wherein the elevated temperature is within the range of about 100°C to about 300°C.

47. The method of claim 30 wherein the elevated temperature is within the range of about 100°C to about 190°C.

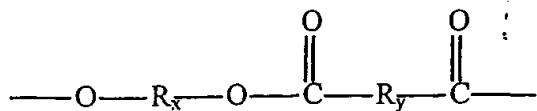
48. The method of claim 30 wherein the elevated temperature is within the range of about 120°C to about 170°C.

49. The method of claim 35 wherein the molar ratio of the macrocyclic oligoester to the cyclic organotin ester is in the range of about 500:1 to about 0.5:1.

50. The method of claim 49 wherein the molar ratio of the macrocyclic oligoester to the cyclic organotin ester is in the range about 50:1 to about 1:1.

51. An organotin copolyester comprising, within its polymeric backbone,

(a) at least one structural unit of formula (I<sub>b</sub>)

(I<sub>b</sub>)

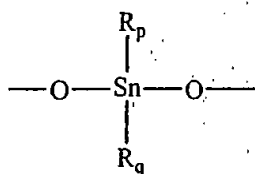
wherein

R<sub>x</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

R<sub>y</sub> is a divalent aromatic or alicyclic group; and

(b) at least one structural unit of formula (III)



(III)

9

10

wherein

11

each of  $\text{R}_p$  and  $\text{R}_q$  independently is a halogen atom or an alkyl group.

1

52. The organotin copolyester of claim 51 wherein  $\text{R}_x$  is one of an ethylene group and a 1,4-butylene group and  $\text{R}_y$  is a divalent benzene group.

2

1

53. The organotin copolyester of claim 51 wherein each of  $\text{R}_p$  and  $\text{R}_q$  independently is a chlorine atom or a butyl group.

2

1

54. The organotin copolyester of claim 51 wherein the molar ratio of structural units of formula (I<sub>y</sub>) to structural units of formula (III) is in the range of about 500:1 to about 0.5:1.

2

3

1

55. The organotin copolyester of claim 54 wherein the molar ratio of structural units of formula (I<sub>y</sub>) to structural units of formula (III) is in the range about 50:1 to about 1:1.

2

1

56. The organotin copolyester of claim 51 wherein the organotin copolyester has a weight average molecular weight of from about 1,000 to about 200,000.

2

1

57. The organotin copolyester of claim 56 wherein the organotin copolyester has a weight average molecular weight of from about 2,000 to about 50,000.

2

1

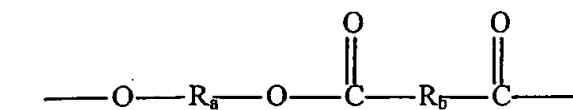
58. A method for polymerizing a macrocyclic oligoester, the method comprising the steps of:

2

(a) providing a macrocyclic oligoester having a structural repeat unit of formula (I<sub>a</sub>):

3

4

(I<sub>a</sub>)

wherein

5

$\text{R}_a$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

6

and

7

$\text{R}_b$  is a divalent aromatic or alicyclic group;

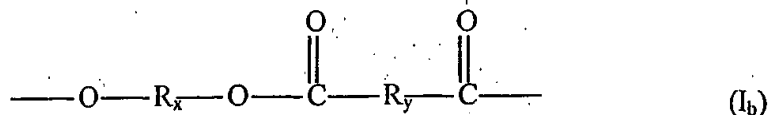
8

(b) providing a polymerization catalyst comprising at least one component compound, wherein the at least one component compound comprises:

9

10

(i) at least one structural unit of formula (I<sub>b</sub>)



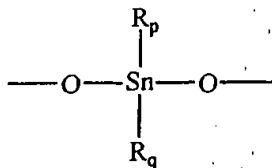
wherein

$\text{R}_x$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

$\text{R}_y$  is a divalent aromatic or alicyclic group; and

(ii) at least one structural unit of formula (III)



(III)

wherein each of  $\text{R}_p$  and  $\text{R}_q$  independently is a halogen atom or an alkyl group; and

(c) contacting the macrocyclic oligoester and the polymerization catalyst at an elevated temperature.

59. The method of claim 58 wherein  $\text{R}_x$  is one of an ethylene group and a 1,4-butylene group,  $\text{R}_y$  is a divalent benzene group, and each of  $\text{R}_p$  and  $\text{R}_q$  independently is a chlorine atom or a butyl group.

60. The method of claim 58 wherein the ratio of structural units of formula (I<sub>b</sub>) to structural units of formula (III) is in the range about 500:1 to about 0.5:1.

61. The method of claim 60 wherein the ratio of structural units of formula (I<sub>b</sub>) to structural units of formula (III) is in the range of about 50:1 to about 1:1.

62. The method of claim 58 wherein the polymerization catalyst comprises at least two component compounds that have a weight average molecular weight of from about 1,000 to about 200,000.

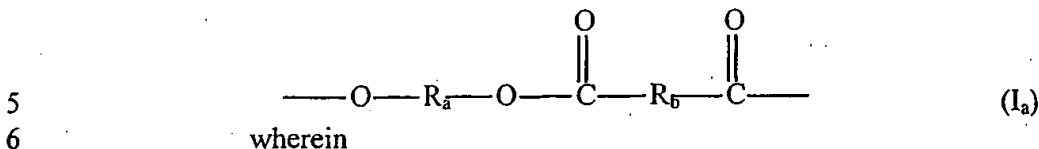
63. The method of claim 62 wherein the polymerization catalyst comprises at least two component compounds that have a weight average molecular weight of from about 2,000 to about 50,000.

64. The method of claim 58 wherein the polymerization catalyst consists of one component compound.

- 45 -

1 65. A method for manufacturing a mixture of a macrocyclic oligoester and a polymerization  
 2 catalyst, the mixture being substantially free from water, the method comprising the steps  
 3 of:

4 (a) mixing an oligoester comprising a structural repeat unit of formula (I<sub>a</sub>):



7 R<sub>a</sub> is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

8 and

9 R<sub>b</sub> is a divalent aromatic or alicyclic group,

10 with an organotin compound;

11 (b) heating the mixture of the oligoester and the organotin compound at an elevated  
 12 temperature;

13 (c) removing water generated during the heating step, thereby obtaining a dried  
 14 reaction mixture of oligoester and organotin compound; and

15 (d) mixing the dried reaction mixture of oligoester and the organotin compound with  
 16 the macrocyclic oligoester.

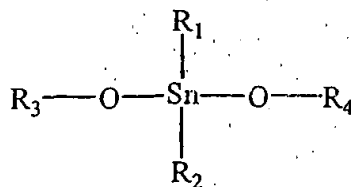
1 66. The method of claim 65 wherein the oligoester is a macrocyclic oligoester.

1 67. The method of claim 65 wherein the organotin ester is a cyclic organotin ester.

1 68. The method of claim 65 wherein the oligoester is a macrocyclic oligoester and the  
 2 organotin ester is a cyclic organotin ester.

1 69. The method of claim 68 wherein the macrocyclic oligoester are selected from the group  
 2 consisting of macrocyclic oligoesters of ethylene terephthalate, propylene terephthalate,  
 3 1,3-propylene terephthalate, 1,4-butylene terephthalate, 1,4-cyclohexylenedimethylene  
 4 terephthalate, ethylene isophthalate, propylene isophthalate, 1,3-propylene isophthalate,  
 5 1,4-butylene isophthalate, 1,4-cyclohexylenedimethylene isophthalate, 1,2-ethylene 2,6-  
 6 naphthalenedicarboxylate, and macrocyclic co-oligoesters thereof.

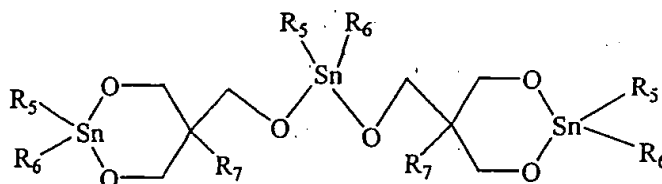
1 70. The method of claim 68 wherein the cyclic organotin compound has the formula (IV),  
 2 (V), or (VI)  
 3



(IV)

wherein

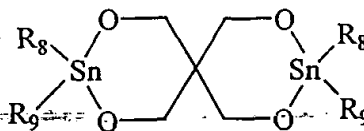
each of  $R_1$  and  $R_2$  independently is a halogen atom or an alkyl group, and each of  $R_3$  and  $R_4$  independently is a hydrogen atom or an alkyl group, or  $R_3$  and  $R_4$  taken together form a cyclic group; or  $R_3-O$  and  $R_4-O$  taken together is an oxygen atom,



(V)

wherein

each of  $R_5$  and  $R_6$  independently is C1-C10 alkyl group, and  $R_7$  is a C1-C4 primary alkyl group, and

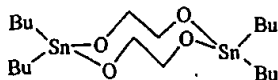


(VI)

wherein

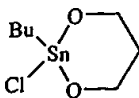
each of  $R_8$  and  $R_9$  independently is a C1-C10 alkyl group.

71. The method of claim 68 wherein the cyclic organotin compound is selected from the group consisting of a compound having the formula of (VIII),



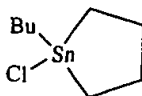
(VIII)

a compound having the formula of (IX),



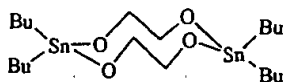
(IX)

6 and a compound having the formula of (X)



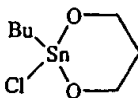
(X).

1 72. The method of claim 68 wherein the macrocyclic oligoester comprises macrocyclic  
2 oligo(1,4-butylene terephthalate) and the cyclic organotin ester is selected from the group  
3 consisting of a compound having the formula of (VIII),



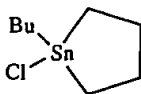
(VIII)

5 a compound having the formula of (IX),



(IX)

7 and a compound having the formula of (X)



(X).

1 73. The method of claim 65 wherein the heating step (b) is conducted at a temperature in the  
2 range of about 100°C to about 190°C.

1 74. The method of claim 65 wherein the heating step (b) is conducted at a temperature in the  
2 range of about 120 °C to about 170°C.

1 75. The method of claim 68 wherein the molar ratio of macrocyclic oligoester to cyclic  
2 organotin ester in step (a) is from about 500:1 to about 0.5:1.

1 76. The method of claim 68 wherein the molar ratio of macrocyclic oligoester to cyclic  
2 organotin ester is from about 50:1 to about 1:1.

1 77. The method of claim 68 wherein the dried reaction mixture of oligoester and organotin  
2 compound has a water content of less than about 2000 ppm.

1 78. The method of claim 77 wherein the dried reaction mixture of oligoester and organotin  
2 compound has a water content of less than about 500 ppm.

## INTERNATIONAL SEARCH REPORT

 Interna Application No  
 PCT/US 02/17607

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C08G63/08 C08G63/40 C08G63/60

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 039 717 A (KAWAKAMI JAMES H ET AL) 13 August 1991 (1991-08-13) column 1, line 12 - line 52 column 3, line 18 - line 29 ---	1-22
A	US 5 648 454 A (BRUNELLE DANIEL JOSEPH) 15 July 1997 (1997-07-15) column 1, line 9 - line 16 column 2, line 3 - column 3, line 2 column 3, line 35 - line 49; claims; examples ---	1-29
A	US 5 661 214 A (BRUNELLE DANIEL JOSEPH ET AL) 26 August 1997 (1997-08-26) the whole document --- -/--	1-29

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "G" document member of the same patent family

Date of the actual completion of the international search

7 August 2002

Date of mailing of the international search report

29 Oct. 2002 (29.10.2002)

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Masson, P

## INTERNATIONAL SEARCH REPORT

 Interna      Application No  
 PCT/US 02/17607

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 680 345 A (KOBAYASHI TAKUMA ET AL) 14 July 1987 (1987-07-14) the whole document ---	20-29
X	DATABASE WPI Week 9243 Derwent Publications Ltd., London, GB; AN 1992-352690 XP002209038 & JP 04 253764 A (TORAY INDUSTRIES) abstract	20-29
X	& PATENT ABSTRACTS OF JAPAN vol. 017, no. 037, 25 January 1993 (1993-01-25) JP abstract	20-29
X	---	
X	DATABASE WPI Week 9745 Derwent Publications Ltd., London, GB; AN 1996-107281 XP002209039 & CN 1 120 555 A (EMS-INVENTA AG) abstract	20-29
P,A	---	
	WO 01 53379 A (WINCKLER STEVEN J ;CYCLICS CORP (US); TAKEKOSHI TOHRU (US)) 26 July 2001 (2001-07-26) the whole document -----	1-29

# INTERNATIONAL SEARCH REPORT

In: ional application No.  
PCT/US 02/17607

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-29

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-29

copolyesters (block or not) containing alkylene dicarboxylate structural units and cyclic esters units (lactones) as structural units  
preparation of such copolyesters by the use of macrocyclic poly alkylene dicarboxylate oligoesters and a transesterification catalyst

2. Claims: 30-78

method for making organotin copolyester by the use and an oligoester and an organotin compound  
organotin copolyester,  
method for polymerizing a macrocyclic oligoester by using a catalyst comprising alkylene dicarboxylate structural units and organotin structural units,  
method for manufacturing a mixture of a macrocyclic oligoester and a polymerization catalyst comprising heating a mixture of an oligoester and an organotin compound

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 02/17607

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5039717	A	13-08-1991	NONE	
US 5648454	A	15-07-1997	NONE	
US 5661214	A	26-08-1997	NONE	
US 4680345	A	14-07-1987	JP 8009661 B	31-01-1996
			JP 61281124 A	11-12-1986
			JP 1808761 C	10-12-1993
			JP 5021134 B	23-03-1993
			JP 62027425 A	05-02-1987
			DE 3667989 D1	08-02-1990
			EP 0208131 A1	14-01-1987
JP 4253764	A	09-09-1992	NONE	
CN 1120555	A	17-04-1996	NONE	
WO 0153379	A	26-07-2001	US 6369157 B1	09-04-2002
			US 2001049430 A1	06-12-2001
			AU 2968901 A	31-07-2001
			EP 1250374 A1	23-10-2002
			WO 0153379 A1	26-07-2001